

**THEORETICAL INVESTIGATION OF APPROACHES FOR OBTAINING
NARROW BAND GAPS IN CONDUCTING POLYMERS**

A THESIS

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FOR
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**By
SERDAR DURDAĞI
August, 2004**

I certify that I have read this thesis and in my opinion it is fully adequate, in scope and in quality, as a thesis of degree of Master of Science.

Assoc. Prof. Dr. Ulrike Salzner (Advisor)

I certify that I have read this thesis and in my opinion it is fully adequate, in scope and in quality, as a thesis of degree of Master of Science.

Assoc. Prof. Dr. Tuğrul Hakioglu

I certify that I have read this thesis and in my opinion it is fully adequate, in scope and in quality, as a thesis of degree of Master of Science.

Assoc. Prof. Dr. Vildan Güner

I certify that I have read this thesis and in my opinion it is fully adequate, in scope and in quality, as a thesis of degree of Master of Science.

Assist. Prof. Dr. Gershon G. Borovsky

Approved for the Institute of Engineering and Sciences

Prof. Dr. Mehmet Baray

Director of Institute of Engineering and Sciences

ABSTRACT

THEORETICAL INVESTIGATION OF APPROACHES FOR OBTAINING NARROW BAND GAPS IN CONDUCTING POLYMERS

SERDAR DURDAĞI

M. S. in Chemistry

Supervisor: Assoc. Prof. Dr. Ulrike Salzner

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Over the last few years, there has been a great deal of research interest in developing organic conjugated polymers with narrow energy band gaps. Narrow band gap polymers would be intrinsically conducting, and thus eliminating the need for doping. There are several approaches for the construction of low band gap systems. Copolymerization of aromatic and o-quinoid heterocycles, minimization of bond length alternation, copolymerisation of donor and acceptor moieties might be most important factors for the lowering the band gap.

The main aim of this work is to determine the reasons for low band gaps and to analyse the major effects, separately.

Recently a number of low band gap systems were synthesized. These systems consist of aromatic donors and quinoid acceptors. To analyse the behaviour of donor/acceptor systems, we performed theoretical studies for these systems. We chose thieno [3,4-b] pyrazine (ThP), F-substituted thieno [3,4-b] pyrazine (F-ThP) and quinoxaline (Qx) as an acceptor and thiophene (Th) and pyrrole (Py) as donor units.

Monomer through octamer of ThP, monomer through tetramer of F-ThP and Qx, were optimised by using density functional theory (DFT). All calculations were performed with the *Gaussian 98* program. For ThP-Th and ThP-Py co-oligomers, energy levels were calculated for monomer through tetramer and, for F-ThP-Py, monomer through trimer data were used. Ionization Potentials (IPs), electron affinities (EAs), band gaps, and band widths of polymers were obtained by extrapolation. IPs and EAs are taken as negative HOMO and LUMO energies.

The order of the band gaps of the homo-polymers is found: F-PThP (1.1 eV) < PThP(1.4 eV) < PQx.(2.4 eV). Band gaps of the systems are found to agree well with the experimental results. We increased the acceptor strength of PThP by adding fluorine units. The band gap is decreased by adding fluorine, however, the valence band width decreased, too.

According to the donor-acceptor concept, we predict narrow band gaps and wider band widths for donor-acceptor co-polymers. However, for ThP-Th and ThP-Py co-polymers, the band gaps are smaller than those of the homo polymers, but there is no increase on conduction band width. ThP-Th and ThP-Py have the same band gap (1.2 eV). The stronger donor pyrrole does not lead to a smaller band gap and wider band widths than the weaker donor thiophene. Thus, there is a contradiction with donor-acceptor concept qualitatively, and also quantitatively.

The results show that, there is no certain correlation between band gaps and inner bond lengths. The bond length alternation (BLA) data are not consistent with the band gap results.

Due to our results, the geometrical mismatch between aromatic and quinoid repeat units forces geometry distortions that impose smaller band gaps.

Overall, we concluded that the situation is more complicated than simple concepts imply and further studies are required before a final conclusion can be reached.

Keywords: Low band gap polymers, density functional theory (DFT), band widths, donor-acceptor concept, conjugate polymers, thieno [3,4-b] pyrazine, quinoxaline, thiophene, pyrrole.

ÖZET

DAR BANT ARALIKLI İLETKEN POLİMERLERİN ELDESİNDE KULLANILAN YAKLAŞIMLARIN TEORİK İNCELENMESİ

SERDAR DURDAĞI

Yüksek Lisans, Kimya Bölümü

Tez Yöneticisi: Doç. Dr. Ulrike Salzner

Ağustos, 2004

Dar bant aralıklı iletken polimerlerin geliştirilmesi için yapılan araştırmalara son birkaç yıldan fazla süredir büyük bir ilgi gösterilmektedir. Dar bant aralıklı polimerler kendiliğinden iletken olduklarından dop edilmeye ihtiyaç duymazlar. Düşük bant aralıklı polimerlerin eldesinde çeşitli yaklaşımlar vardır. Aromatik ve o-qunoid heterosiklik yapıların kopolimerizasyonu, sıralı bağ değişim uzunluğu, verici ve alıcı yapıların kopolimerizasyonu bant aralığının düşürülmesi için en önemli etkenler olarak sayılabilir.

Bu çalışmada ana amaç, düşük bant aralığının nedenlerini araştırmak ve buna neden olan önemli faktörleri ayrı ayrı analiz etmektir.

Son zamanlarda, düşük bant aralıklı bazı polimerler sentezlenmiştir. Bu sistemler aromatik verici ve qunoid alıcı gruplar içerirler. Verici/alıcı sistemlerin davranışlarını analiz etmek için, bu sistemlerin teorik çalışmalarını yaptık. Tiyeno [3,4-b] pirazin (ThP), F-değişkenli tiyeno [3,4-b] pirazin (F-ThP) ve qunoksaline (Qx) alıcı ve tiyofen (Th) ile pirol (Py) birimlerini verici olarak kullandık.

ThP'nin monomerinden oktamerine, F-ThP ve Qx'in monomerlerinden tetramerlerine kadar birimler yoğunluk fonksiyonel teorisi (DFT) kullanılarak optimize edildi. Bütün hesaplamalar için *Gaussian 98* programı kullanıldı. ThP-Th ve ThP-Py ko-oligomerlerinde enerji seviyeleri monomerden tetramere, F-ThP-Py için de monomerden trimere kadar veriler kullanıldı. Polimerlerin iyonlaşma potansiyelleri (IP), elektron ilgileri (EA), bant aralıkları, ve bant genişlikleri ekstrapole edilerek elde edildi. IP ve EA, HOMO ve LUMO enerjilerinin negatif değerleri olarak alındı.

Homopolimerlerin bant aralık sırası : F-PThP (1.1 eV) < PThP(1.4 eV) < PQx.(2.4 eV) olarak bulunmuştur. Bu sistemlerin bant aralıkları deneysel değerler ile uygunluk göstermektedir. PThP'nin akseptör özelliğini flor grupları ekleyerek arttırmaya çalıştık. Flor eklenmesi ile bant aralığı azaldı ancak değerlik bant genişliği de azaldı.

Verici-alıcı konsepte göre, verici/alıcı ko-polimerlerinde, düşük bant aralığı ve geniş bant genişlikleri oluşmasını öngördük. Ancak, ThP-Th ve ThP-Py ko-polimerleri için, düşük bant aralığı bulmamıza rağmen, iletken bant genişliğinde bir artma olmadığını gördük. ThP-Th ve ThP-Py aynı bant aralığına (1.2 eV) sahiptir. Tiyofen'e göre daha güçlü bir verici olan pirol daha düşük bant aralığı ve daha büyük bant genişliğine neden olmamıştır. Dolayısıyla, burada verici/alıcı konsepti ile hem kalitatif hem de kuantitatif bir çelişki söz konusudur.

Bant aralığı ile iç bağ uzunluğu arasında herhangi kesin bir korelasyonun olmadığını hesaplama sonuçlarımızdan anlıyoruz.. Bağ uzunluk değişimi (BLA) verileri ile bant aralık sonuçları arasında herhangi beklenen bir uyum yoktur.

Sonuçlarımıza göre, aromatik ve qunoid tekrarlayan birimler arasındaki uygun olmayan geometrik eşleşmeler, geometride bozulmalara neden olur ve bu da düşük bant aralığının oluşmasını sağlar.

Sonuçta, oldukça komplike bir durumla karşı karşıya olduğumuzu ve kesin yargılara varmadan önce bu konu üzerinde daha fazla çalışma yapılması gerektiği kararına vardık.

Anahtar kelimeler: Düşük bant aralıklı polimerler, yoğunluk fonksiyonel teorisi (DFT), bant genişlikleri, verici-alıcı konsepti, konjuge polimerler, tiyeno [3,4-b] pirazin, qunoksaline, tiyofen, pirol.

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Chapter 1. Introduction

1.1 Motivation

In attempting to find an organic polymer that would be a "metal" or that would at least have a partial metallic character, a lot of studies have been done for about more than 20 years. From the early days of study of conducting polymers scientists envisaged that there might be a class of these polymers, that would have either a zero band gap (a single and continuous band consisting of the valence and conduction bands) or a very low band gap. In material science, band structure engineering has become important since the band gap (E_g) is one of the most important factors for controlling the physical properties. Especially the design of low band gap polymers ($E_g < 1.0$ eV) is a major challenge in the field of conducting polymers.

It is the purpose of this chapter to review and discuss research on low band gap systems.

1.2 Low Band Gap Conducting Polymers

The energy band gaps obtained from band structure calculations for solids are analogous to highest occupied molecular orbital (HOMO)- lowest unoccupied molecular orbital (LUMO) energy differences in molecules. (Figure 1.2.1). ^[1]

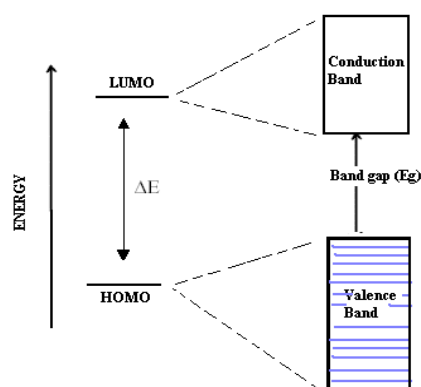


Figure 1.2.1 Relationship between HOMO-LUMO gaps of finite and band gaps of the infinite system

An energy band is actually made up of an infinite number of discrete "energy states". At room temperature, all the lowest energy levels are filled, however all the upper energy levels are empty. As we progress from lower to higher levels, we reach a particular set called the valence band (completely filled in a pure semiconductor) and the conduction band (empty in a pure semiconductor). The conduction band is normally the one in which the electrons contribute to conduction of electric current. Electrons move to empty energy levels in response to an electric field, irradiation, or thermal energy, if the band gap is small.

If the band gap is very large, very few electrons can be excited across the band gap and be in the conduction band because the average thermal energy of any particle at room temperature is only about 0.025 eV ^[28]. Carbon in its crystalline diamond form is an insulator. However, in silicon, many more electrons are in the conduction band because its band gap is only 1.1 eV. In an insulator there are no electrons in the conduction band and the next lowest, the valence band, is completely filled. In a metal, however, the conduction band is partially filled at all temperatures, thereby allowing conduction by the free electrons.

Reduction of the band gap can increase the thermal population of the conduction band and thus enhance the number of intrinsic charge carriers. Narrow band gap polymers are very important because they can be candidates for the intrinsically conducting polymers. Intrinsically conducting polymers are conducting π -conjugated polymers that do not need additional doping and are characterized by electrically neutral conjugated systems. Band gaps below 0.5 eV are considered to be required for intrinsic conductivity.

The red shift of the absorption and emission spectra resulting from a decrease of band gap can make available conjugated polymers and they can have good transparency in the visible spectrum and they might be useful as IR sensors/detectors ^[2]. Moreover, they might give a clue for real intrinsically metallic organic polymers ^[3].

1.2.1 Polyacetylene

Trans-polyacetylene, (trans (-CH)_n) (Figure 1.2.2) is the first highly conducting organic polymer. Shirakawa et al. ^[4] have achieved synthesizing flexible copper-coloured films of the *cis*-isomer and silvery films of the *trans*-isomer of polyacetylene in the presence of Ziegler catalyst. These polymers are semiconductors. A semiconductor is characterized by a small energy gap between a filled valence band and an empty conduction band. In many semiconductors, called extrinsic semiconductors, the size of the band gap is controlled by carefully adding impurities, the process called *doping*. Undoped Polyacetylene has band gap of 1.4 eV. The conductivity of *trans*-polyacetylene [σ (273K)= $4.4 \cdot 10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$] is higher than that of *cis*- isomer [σ (273K)= $1.7 \cdot 10^{-9} \Omega^{-1} \cdot \text{cm}^{-1}$]^[4].

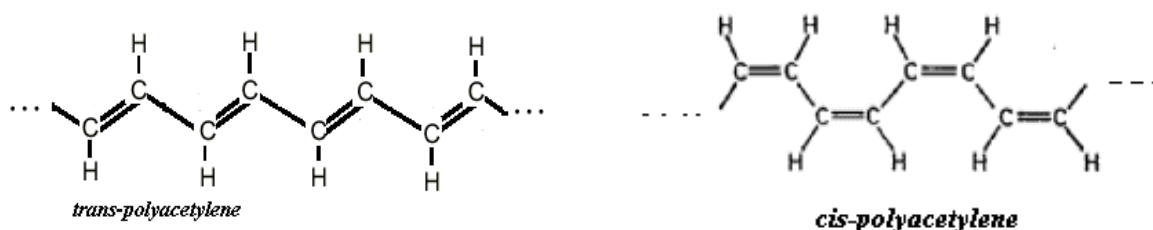


Figure 1.2.2 *trans*- and *cis*- isomers of polyacetylene

Trans-polyacetylene has a degenerate ground state. The difference between polymers with and without degenerate ground state can be easily visualized, if the energy of the two possible structures is plotted as a function of the distortion parameter for a spatially uniform bond arrangement (Figure 1.2.3) ^[5].

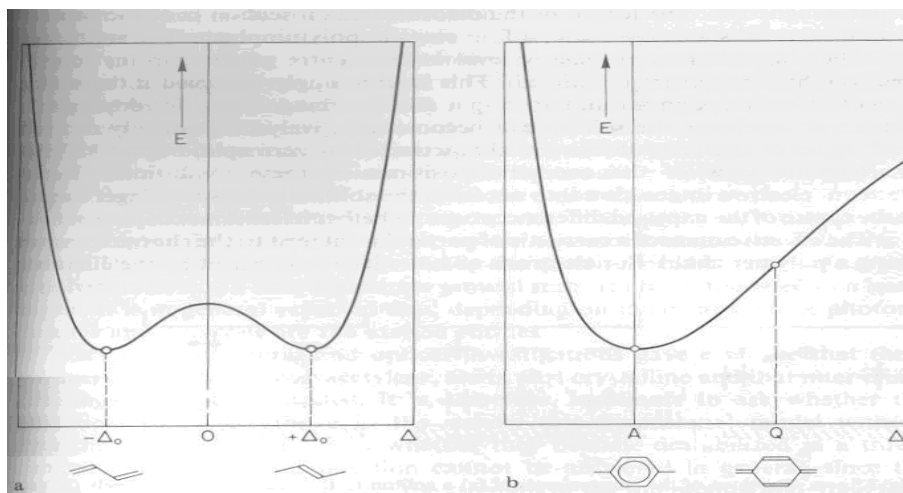


Figure 1.2.3 Ground state energy as a function of the configuration coordinate for a system with a degenerate ground state, such as trans- $(\text{CH})_n$ **(a)**, and a single ground state **(b)**

Polymers with a degenerate ground state are susceptible to a defect that is not present in other polymers. This defect results in mobile unpaired electron on the backbone, however the total charge does not change. This newly formed defect state, referred as "soliton" produces a new energy level at mid-gap^[6]. For a neutral soliton the mid-gap state is singly occupied. (Figure 1.2.4).

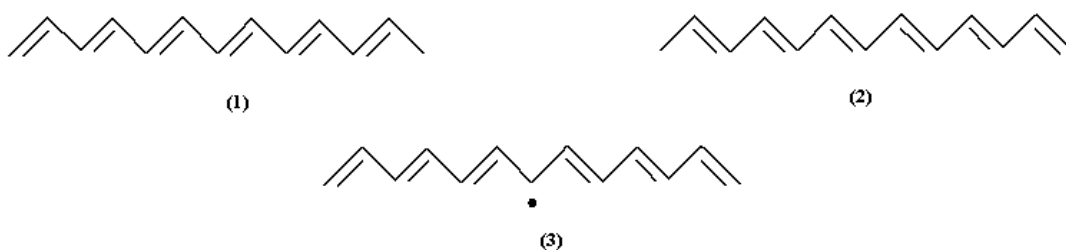


Figure 1.2.4 Degenerate ground state of cis-polyacetylene (1), (2). A soliton defects at a phase boundary between the two degenerate levels (3).

The mid-gap state can be also empty or doubly occupied producing a positively or negatively charged soliton. In an even numbered chain, solitons can only form in pairs. Also, a positively charged soliton can combine with a neutral soliton and form radical cation, also called "polaron"^[6]. A polaron can travel down the molecule. (Figure 1.2.5).

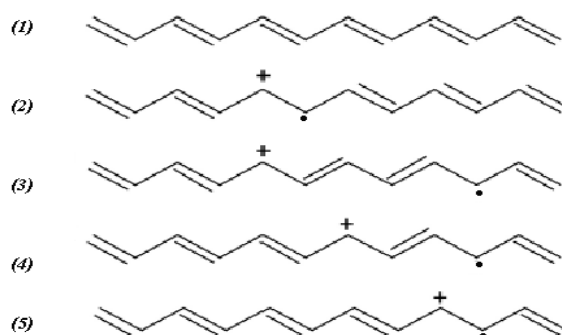


Figure 1.2.5 The polaron migration at trans-polyacetylene

1.2.2 Polyheterocycles

The synthesis of polyacetylene was a starting point for a considerable number of studies. Electrodeposition of free standing films of polypyrrole from organic environment opened a new way to research on polyheterocyclic and polyaromatic conducting polymers^[7,8]. After the oxidation of polypyrrole, aromatic systems have been synthesized for producing conducting polymers. (Table 1.2.1)

Polymer	Structure		Polymer	Structure
Polypyrrole			Polyindole	
Polythiophene			Polyaniline	
Polyfuran			Polyazulene	
Polyisothianaphthane			Poly <i>para</i> -phenylene	

Table 1.2.1 Some of most widely researched polyheterocycles

Heterocyclic polymers such as polythiophene, polypyrrole, polyaniline, and many substituted, multi-ring and polyaromatic systems have a conjugated backbone, which is required for electroactivity.

Polyaromatic polymers have non-degenerate ground states since the two mesomeres e.g. aromatic (Figure 1.2.6.a) and quinoid (Figure 1.2.6.b) are not energetically equivalent ^[9]. Another difference between polyacetylene and polyaromatic π -conjugated polymers is the aromaticity of the latter, which results in a competition between π -electron confinement within the rings and delocalisation along the main chain.

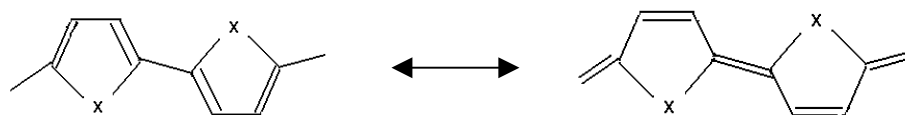


Figure 1.2.6 a. aromatic form

b. quinoid form

The success with designing polyisothianaphtane (PITN), which has 1.1 eV band gap (about 1 eV lower than polythiophene) showed that band gaps might be tuned by structural modification ^[10]. This led to a lot of theoretical and experimental investigations with the aim of exploring the correlation between the structures and band gaps of polymers.

1.2.3 Peierls Distortions

Peierls distortion is the distortion of a regular one-dimensional structure with a partially occupied band to give bond alternation, also called dimerization. Bond length alternation in the main chain is an important contribution to the existence of a finite E_g value in π -conjugated polymers.

A Peierls distortion opens a gap at the Fermi level, producing a net stabilization of the distorted structure. The Peierls distortion for chain compounds is analogous to the *Jahn-Teller effect*^[55,56] for molecules.

Due to the Jahn-Teller theorem, there must be a large interaction with electronic and vibrational motions of two unpaired electrons in degenerate orbitals. Therefore, there must be at least one normal mode of vibration that breaks degeneracy and lowers the energy and the symmetry^[11]. Figure 1.2.7^[11] shows the lowering the symmetry from D_{4h} to D_{2h} , thus localization of double bonds. Lowering the symmetry leads to breaking of an orbital degeneracy, stabilizing one orbital and destabilizing the other.

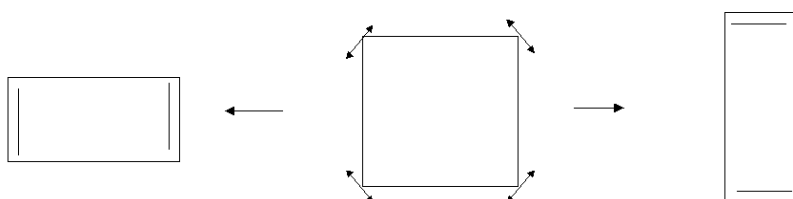


Figure 1.2.7 Lowering the symmetry from D_{4h} to D_{2h} leads to localization of double bonds.

The prototypical example of the Peierls distortion in polymer chemistry is the bond alternation present in polyacetylene (Figure 1.2.8).



Figure 1.2.8 Peierls distortion leads to either the neighboring atoms alternately get slightly closer and further apart.

1.3 Conductivity

Conductivity is not only the result of charge transfer along the backbone, but it is also due to electron transfer between chains and between different conjugated fragments of the same chain. The conductivity of a conjugate polymer may be described by equation 1.3.1^[12].

$$\sigma = \sum n_i Z_i e v_i / E \quad (\text{Equation 1.3.1})$$

where,

σ = conductivity (S. cm^{-1})

n_i = number of charges carried by each type

Z_i = carrier type

e = electronic charge ($1.6 \times 10^{-19} \text{ C}$)

v_i = drift velocity of electron (cm.s^{-1})

E = electric field

1.4 Approaches to Narrow Band Gap Polymers

There are several powerful approaches towards construction of smaller band gap systems. One of them is copolymerisation of aromatic and *o*-quinoid heterocycles that leads to narrow band gap by reducing bond length alternation. Another approach is the alternation of electron donor and acceptor (D-A) units in the π -conjugated polymer chain. Donor-like structures are found in hetero ring systems with N, O or S atoms ^[3]. In this way, one may increase the HOMO level and decrease LUMO level. Finally, π -conjugation length along the polymer backbone and the steric interactions between adjacent units relating to co-planarity are also important factors that affect the band gaps of polymers.

1.4.1 Minimization of Bond Length Alternation

Polythiophene has wide band gap ($\sim 2\text{eV}$) because it has small quinoid structure contribution in its ground state, resulting in significant single bond character of the thiophene-thiophene linkages and therefore a large bond length alternation. Increasing the double bond character of the thiophene-thiophene linkage can be accomplished by making the quinoid like structure energetically more favourable ^[13]. This is the case in polyisothianaphthene (PITN) (Figure 1.4.1). Structures inducing quinoid character in the ground state of the conjugated polymers tend to decrease the band gap.

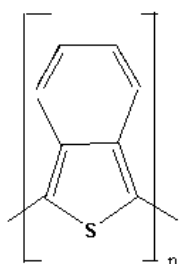
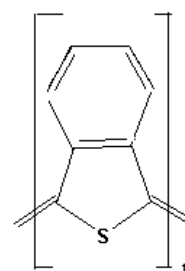


Figure 1.4.1 a. Aromatic PITN



b. Quinoid PITN

1.4.2 Copolymerization of Aromatic and o-Quinoid Heterocycles

Copolymerization (Figure 1.4.2) of aromatic and o-quinoid heterocycles, causes minimization of bond length alternation and this leads to narrower band gaps. The electronic properties of copolymers are usually intermediate between those of its components. Thus, the properties can be tuned by varying the molecular composition of the copolymer and by arranging the components in the chain ^[14-19].

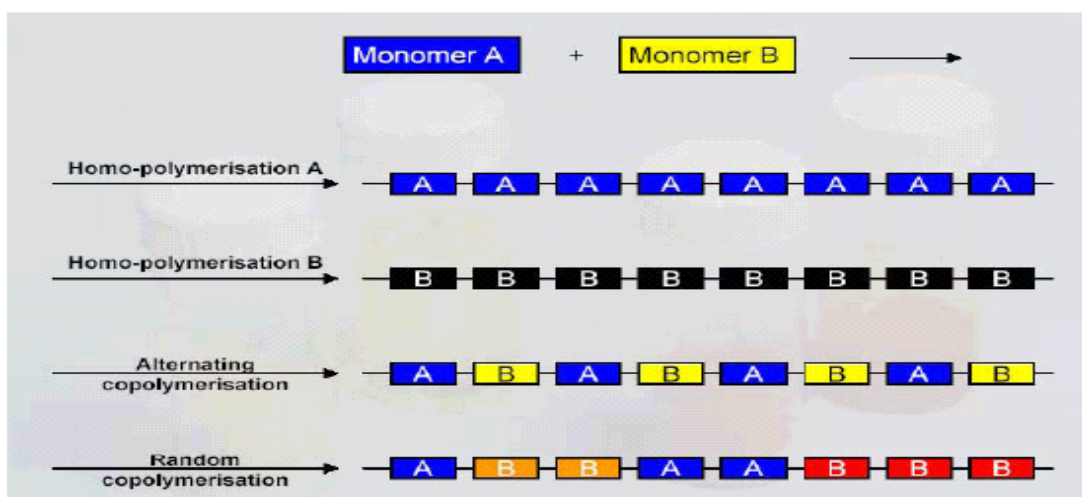


Figure 1.4.2 Copolymers can evaluate by alternatingly or randomly.

1.4.3 Donor-Acceptor Concept

Havinga et al. proposed the donor-acceptor concept for construction of narrow band gap conducting polymers in 1993 ^[3]. This concept predicts polymers with repeat units originating from a donor with high lying energy levels and an acceptor with low lying energy levels, to have narrow band gaps and wider band widths ^[20, 27]. Since wide band widths are needed for high on chain mobility and narrow band gaps for intrinsic conductivity, Havinga's idea led to increased interest in donor-acceptor systems.

The underlying thought is that the polymer valence band forms energetically near the HOMO of the donor and that the conduction band forms in the region of the LUMO of the acceptor (Figure 1.4.3). Thus, conjugated polymers with donor and acceptor moieties in the main chain have been claimed to have the lowest band gap for a combination with the highest electronegativity difference between donor and acceptor groups.

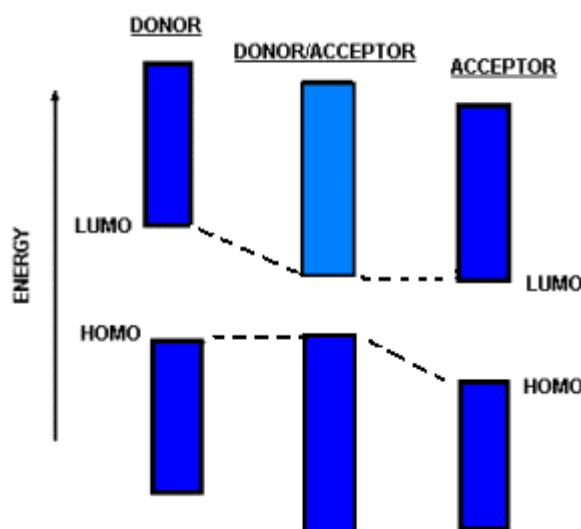


Figure 1.4.3 Changing of band gap and band widths with composition of donor-acceptor structures

However, it should be noted that conductivity of homopolymers is better than that of the donor-acceptor systems. Doping of homopolymers can yield an increase in conductivity of 15 orders of magnitude. In donor-acceptor systems conductivity increases by just 2-5 orders of magnitude ^[20]. Thus, although intrinsic conductivities are higher in donor-acceptor systems, conductivity of doped forms is lower than that of homopolymers.

A lot of examples of polymers belonging to the class of π -conjugated D-A systems are known that do not show a lower band gap than that of the classical low band gap polymer polyisothianaphthene (1.1 eV) ^[21-23]. But, Tanaka et al. have shown that the application of the electron-donor thiophene unit in the combination with benzo [1,2-c:4,5c']-bis[1,2,5]thiadiazole- or thieno[3,4-b] pyrazine-derived electron-acceptor units produces conjugated copolymers that have the lowest band gaps reported so far ^[24].

π -conjugated heteroaromatic copolymers consisting of electron-releasing thiophene and electron-withdrawing pyridine units show unique optical and electrochemical properties due to an intramolecular charge transfer between thiophene and pyridine moieties ^[25].

To summarize, there are several factors that effect the band gap: ^[2]

$$E_g = E^{\delta r} + E^{\theta} + E^{\text{res.}} + E^{\text{sub.}} + E^{\text{int.}}$$

Here $E^{\delta r}$ is the bond length alternation along the chain, E^{θ} is the mean deviation from planarity, $E^{\text{res.}}$ is the aromatic resonance energy of the ring, $E^{\text{sub.}}$ is the inductive or mesomeric electronic effects of substituents, and $E^{\text{int.}}$ is the inter-chain or inter-molecular coupling in the solid state.

Aromatic resonance energy of the ring and electronic effects of heteroatoms are major contributions to the final value of E_g . Therefore, one can tune the band gap by playing with these factors.

1.5 Counter Arguments to Donor-Acceptor Concept

When donor-acceptor systems are formed, they have small band gaps if there is weak interaction between the two units. If there is strong interaction, charge transfer increases the band gap. On the other hand, weak interactions lead to narrow rather than wide valence and conduction bands. This is because the interaction between the energetically different fragments (in repeating unit) is weak and it should cause small dispersion of the bands. The effect of strong and weak interacting molecules to band gaps and band widths is shown by Figure 1.5.1. Narrow bands can explain the smaller conductivities of donor-acceptor systems upon doping compared to homopolymers. Salzner et. al.^[20] concluded that donor-acceptor concept does not work in principle. In general, the prediction of small band gaps in combination with wide valence and conduction bands seems unrealistic from a theoretical point of view.

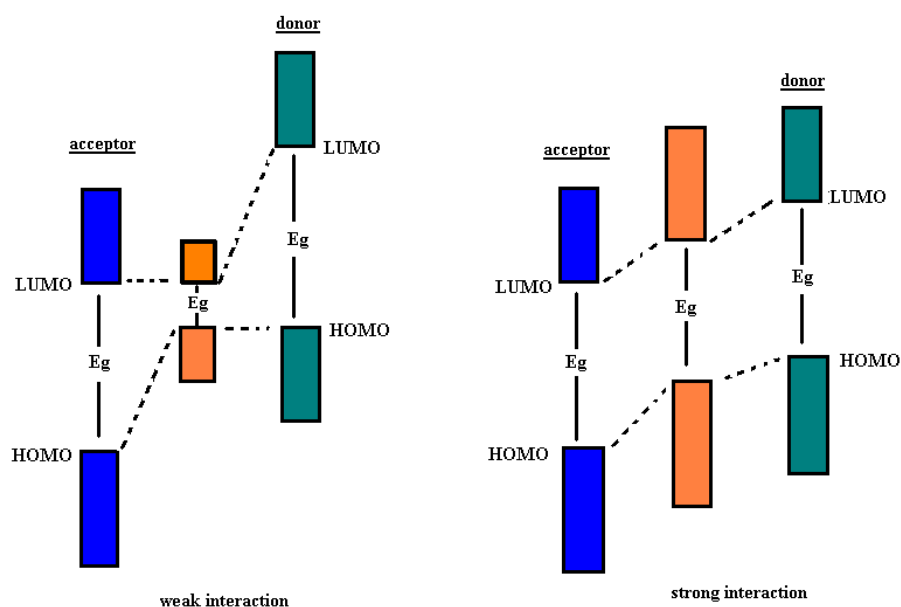


Figure 1.5.1 Strong and weak interactions of molecules

1.6 Investigated Systems

Recently a number of narrow band gap systems have been synthesized. They consist of aromatic donors and quinoid non-classical acceptors. Since the band gap reduction compared to either homopolymer was attributed to the donor-acceptor concept, we started theoretical investigations with the aim of analysing the influence of donor-acceptor substitution.

We chose thieno [3,4-b] pyrazine (ThP), F-substituted thieno [3,4-b] pyrazine (F-ThP) and quinoxaline (Qx) as acceptors and thiophene (Th) and pyrrole (Py) as donor units (compare Figure 1.6.2). Energy levels of molecules (ionization potentials, IPs and electron affinities, EAs) are important parameter for selection of acceptor and donor groups. For instance, we chose pyrrole as donor and thieno [3,4-b] pyrazine as acceptor group since pyrrole has higher energy levels. (Figure 1.6.1)

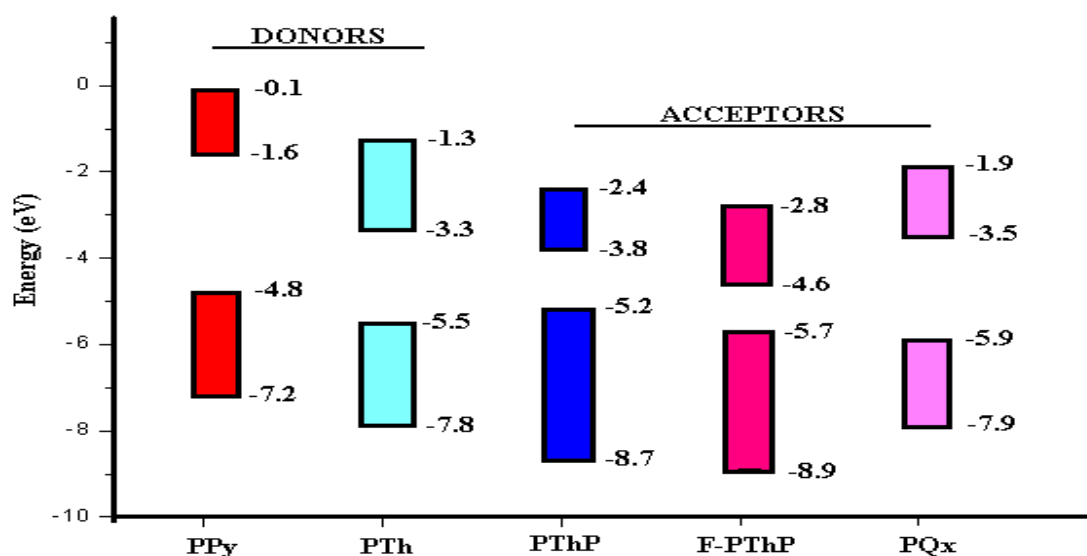
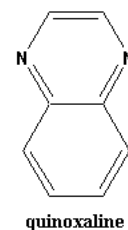
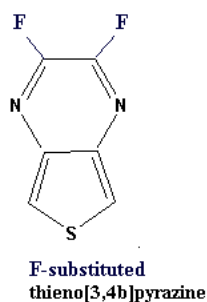
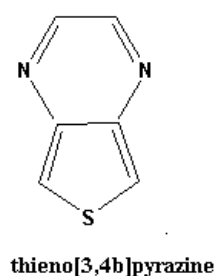


Figure 1.6.1 Energy levels for donor and acceptor systems

Data for thiophene and pyrrole are taken from a previous study, carried out at the same level of theory ^[51, 52]. IPs and EAs of ThP, F-ThP, and Qx oligomers are plotted against to $1/n$ (n , number of oligomers), and polymeric IPs and EAs are obtained by extrapolation, as described in more detail in the results and discussion chapter.

Acceptors



Donors

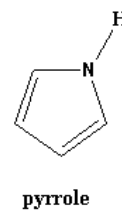
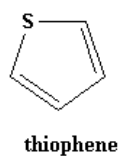


Figure 1.6.2 Investigated acceptor and donor units

Thieno [3,4-b] pyrazines have been shown to be excellent precursors for the production of low band gap conjugated polymers. Theoretical calculations by Lee and Kertesz^[57], Karpfen and Kertesz^[58], Kurti et.al.^[59] Nayak and Marynick^[60], Kastner et al.^[61], and Hoogmartens et al.,^[62] have shown that polyisotianaphtane (PITN) and polythieno[3,4-b]pyrazine (PThP) have quinoid ground states^[50] (Figure 1.6.3).



Figure 1.6.3 Aromatic quinoid forms of PThP

The systems investigated here are comprised of donor-acceptor systems, the donor being aromatic, the acceptor being quinoid. Since thiophene and pyrrole prefer aromatic structures, and thieno [3,4-b] pyrazine prefers a quinoid structure, a geometric mismatch results upon copolymerisation. Such structural mismatch decreases bond length alternation since quinoid structures have single bonds where aromatic structures have double bonds. Since bond length alternation is one of the important factors responsible for narrow band gaps, alternating quinoid and aromatic repeat units might decrease the band gap.

Firstly, we investigated ...D-A-D-A-D-A... (1:1 donor/ acceptor ratio). Then we increased the donor ratio to see the effect of donor/acceptor ratio to the i.e. band gap, band widths, and bond length alternation. Thus, copolymer has the following chain structure for 2:1 donor/acceptor ratio: ...D-A-D-D-A-D-D-A-D....

Figure 1.6.4 and 1.6.5 show the structures of 1:1 and 2:1 ratio donor-acceptor systems, respectively.

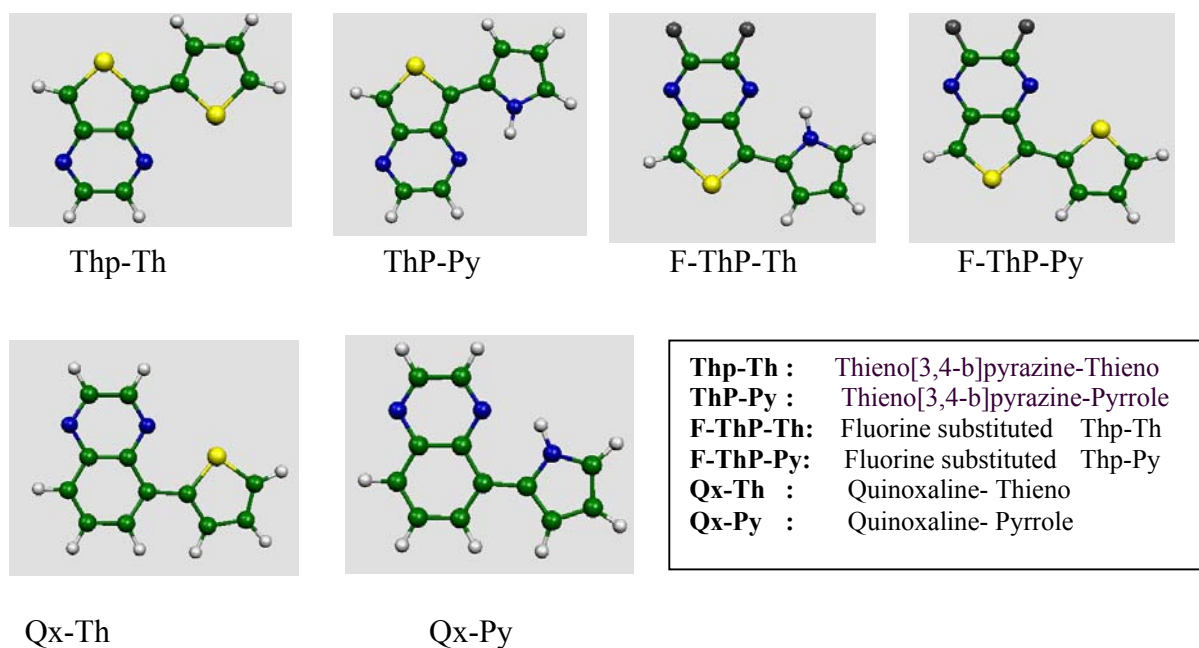


Figure 1.6.4 1:1 ratio donor/acceptor systems

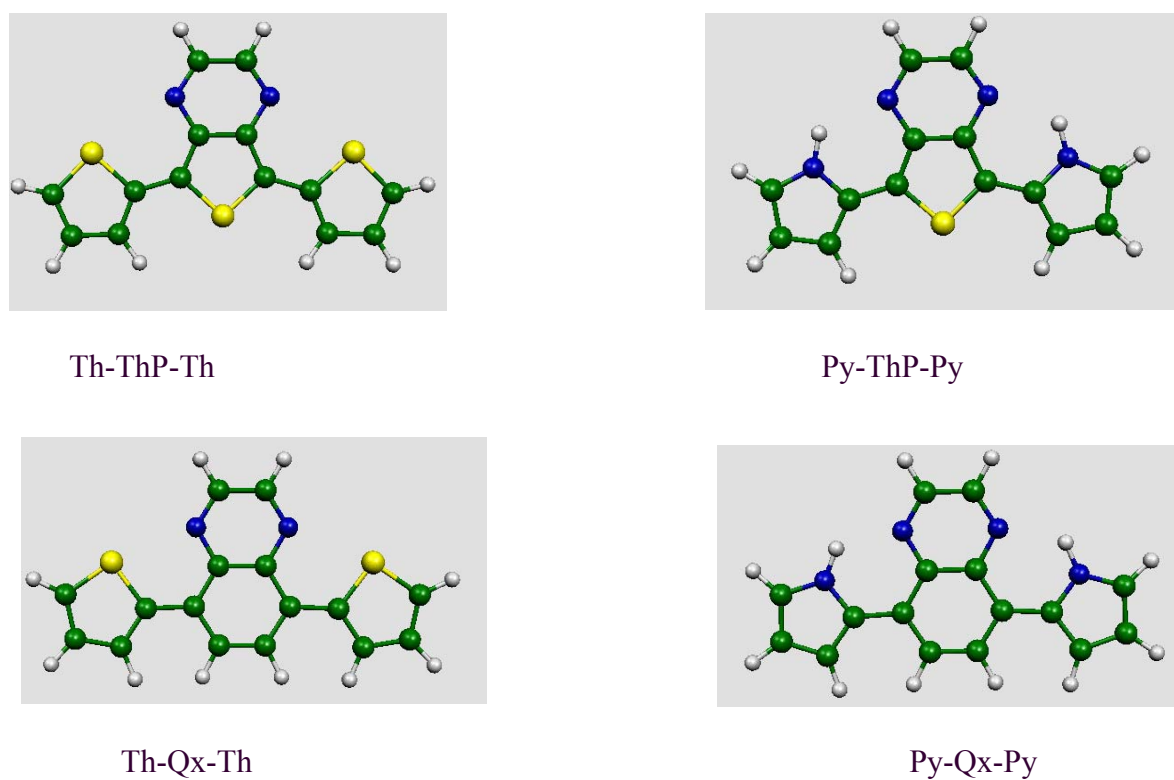


Figure 1.6.5 2:1 ratio donor/acceptor systems

1.7 What is Our Aim?

Our aim is to determine the reason for the small band gaps and to separate effects due to mixing of quinoid and aromatic structures, due to bond length alternation, and due to donor-acceptor concept.

Chapter 2. Theoretical Background

2.1 Some Useful Definitions for Many-Body Systems

There are many approaches of computational chemistry that are popular in molecular modelling. We can divide these approaches to two broad part, *empirical* and *quantum approaches* ^[31]. Empirical approaches use simple models of harmonic potential, electrostatic interaction, and dispersion forces for basic comparisons of energetics and geometry optimisation. Quantum approaches roughly divided into *semi empirical methods* and *non-empirical (or ab initio) methods*. Semi empirical methods are the approximate methods in which some quantities are taken from experiment, some small quantities are neglected, and some quantities are estimated by fitting to experimental data. Ab initio methods do not require empirical parameters and can be used for a lot of molecular systems. Ab initio methods use the Hartree- Fock method as a starting point, i.e., the wave function is used to describe electronic structure. Lately, density functional approaches have come into major use at the non-empirical methods ^[31].

The principles of density functional theory of electronic structure are conveniently expounded by making reference to conventional wave function theory. Therefore, it is worthwhile briefly reviewing several key concepts, and developing a systematic nomenclature and notation, so the remainder of the chapter is devoted to this aim. Then the next part summarizes the details of density functional theory.

Approach to quantum mechanic postulates the fundamental principles and then uses these postulates to deduce experimental results ^[29]. For the definition of the *state* of a system in quantum mechanics, the function of the coordinates of particles referred as the *wave function* or *state function* Ψ ^[29]. In general, the state changes with time, thus for one-particle, one-dimensional system, we have $\Psi=\Psi(x, t)$. The wave function contains all possible information about a system. ^[29]

Suppose we have a single particle for instance an electron of mass m moving in a field of space under the influence of a potential V ^[63]. To find the future state of a system from knowledge of its first state, we need an equation that tells us how the wave function changes with time. The particle is described by a wave function $\Psi(x, t)$ that satisfies *Schrödinger's time dependent equation*, ^[29]

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x) \Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t} \quad \text{(Equation 2.1.1)}$$

(where the $\hbar = h/2\pi$, h is Planck's constant, and $i^2 = -1$)

The time-dependent Schrödinger equation might look very complicated, however many applications of quantum mechanics to chemistry use the simpler time-independent Schrödinger equation ^[29].

$$\frac{-\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} + V(x) \Psi(x) = E \Psi(x) \quad \text{(Equation 2.1.2)}$$

Equation 2.1.2 is the *time-independent Schrödinger equation* for a single particle of mass m moving in one dimension, and E is the energy of the system.

For the hydrogen atom, the exact wave function is known. For helium and lithium, very accurate wave functions have been calculated by including interelectronic distances in the variation functions. Because of the inter-electronic repulsion term, the Schrödinger equation cannot be solved exactly for higher atomic numbers ^[29, 64, 65, 66].

Hartree-Fock theory is a good approximation to solution of the many-body problem. Instead of calculating repulsions between electrons explicitly, repulsions are calculated between one electron and the average field of all of the other electrons. Therefore, that electrons avoid each other cannot be treated. Therefore, Hartree-Fock energies are too high, since electrons can get too close to each other, so high interactions e.g., Coulomb repulsions, are overestimated ^[29, 64].

In the 1930s Hartree and Fock developed a systematic procedure to finding the best possible forms of orbitals. A variational wave function that is an antisymmetrized product of the best possible orbitals is called Hartree-Fock wave function. Hartree and Fock showed that the Hartree-Fock orbitals, Φ_i satisfy equation: ^[65-67]

$$\mathbf{F}.\Phi_i = \epsilon.\Phi_i \quad \text{(Equation 2.1.3)}$$

where, F is Hartree-Fock operator, and ϵ is energy of i^{th} Hartree-Fock orbital.

Hartree-Fock orbitals were calculated numerically and the results expressed as a table of values of Φ_i at various points in space. In 1951 Roothaan showed the most convenient way to express Hartree-Fock orbitals is as a linear combination of a set of functions called *basis functions* ^[29]. Starting in the 1960s, the use of electronic computers allowed Hartree-Fock wave functions for many molecules to be calculated. If sufficient basis functions are included, one can get molecular orbitals that differ negligibly from the true Hartree-Fock molecular orbitals. Any set functions can be used as basis functions, as long as they form a complete set. However, molecules are made of bonded atoms, and it must be convenient to use atomic orbitals as the basis functions. Each molecular orbital is then written as a linear combination of the basis set of atomic orbitals and the coefficient of the atomic orbitals is found by solving the Hartree-Fock equations. Basis set is the set of mathematical functions from which the wave function is constructed ^[29, 64].

The complete set of basis functions used in atomic Hartree-Fock calculations is the set of *Slater Type Orbitals* (STOs) ^[63]. STOs resemble hydrogen atomic orbitals. However, they suffer from a fairly significant limitation ^[65, 67, 68]. There is no analytical solution for the general four-centre integrals when the basis functions are STOs ^[29, 63, 64]. The requirement that such integrals be solved by numerical methods, Boys and McWeeny to propose an alternative to the use of STOs in the 1960s ^[63]. All that is required for there to be an analytical solution of the general four-index integral formed from such functions is that the radial decay of the STOs be changed from $e^{-\zeta r}$ to $e^{-\zeta r^2}$, that is using gaussian type functions (GTOs) ^[64, 65, 67, 68].

The quality of a basis set can be increased by the addition of extra basis functions. Important additions to basis sets are *polarisation functions* and *diffuse functions* ^[29, 64].

When bonding occurs, atomic orbitals are distorted from their normal spatial representation. Polarisation functions (represented by a star) can be added to basis sets to reproduce the effects of such distortion. Polarisation functions are p- or d-type basis functions that are added to describe the distortion of s or p-orbitals, respectively ^[29, 63, 64]. In excited states and in anions, the electronic density is spread out more diffuse. To model this correctly, basis functions with small exponents have to be used. These additional basis functions are called diffuse functions (represented by +).

Any wave function obtained by solving the Hartree-Fock equation is called a *Self Consistent Field* (SCF) wave function (meaning that the field experienced by an atom depends on the global distribution of atoms)^[65, 68]. The basic idea of the SCF method is simple. By making an initial guess for the spin orbitals, one can calculate the average field for a new set of spin orbitals. By using these new spin orbitals one can obtain new field and repeat the procedure until self-consistency is reached. (Until the fields no longer changes).

The fundamental assumption of Hartree-Fock theory, that each electron sees all of the others as an average field allows for tremendous progress to be made in carrying out practical molecular orbital calculations. However, neglect of electron correlations can have profound chemical consequences when it comes to determining accurate wave functions. The Hartree-Fock method is usually problematic for reaction energies, because reactants and products differ substantially in their electronic distributions ^[29, 65, 68].

From the late 1960s onward these terms found some formal reasonably in a theory of energy and force in electronic structure systems called *density functional theory*.

2.2 Basics of Density Functional Theory (DFT)

One of the main problems of quantum methods in chemistry is including short-range correlations into self-consistent field theory^[31-33,36]. Short-range correlations involve the local environment around a particular atom and are much more difficult to treat. Fortunately, the fine details of short-range correlations are often of only minor importance so that a theory based on the concept of a self-consistent field is sufficiently accurate for many purposes. This is not the case for strongly correlated systems, implying that the short-range correlations between electrons due to exchange and their mutual Coulomb repulsions must be accounted for very accurately if even the qualitative features of observed behaviour are to be reproduced^[31-33,36].

Several promising methods of dealing with the problem of strong correlations have been developed in recent years. Kohn and Sham made one of the important advances in the calculation of the energy of density of atoms and the forces on each atom in 1965^[33]. They showed how a self-field consistent theory could be applied to this problem. In their method, electron density plays an important role so that, although the term has more general applicability, the Kohn-Sham method is commonly referred to as density functional theory (DFT).

DFT is today one of the most important tools for calculating of ground state properties of metals, semiconductors, and insulators^[70]. The principal aim of any many-body theory is to reduce the number of parameters needed to describe the system. In such a system, which may contain anywhere between 2 and may be more than 10^{23} particles, each particle is described by its three coordinates in space, which may be time-dependent, and possibly a spin coordinate. So, it involves great expense to solve the equations of motion of such a system^[30,32].

It is imperative to say that, density functional theory is only able to predict the ground state energy and properties. Since the ground state energy is a function of a number of parameters of the system, we may also use density functional theory to find other ground state properties such as bond lengths and angles.

In principle, DFT is able to produce these quantities exactly, however, in application it is necessary to introduce some approximations^[30]. Fortunately, even the simplest reasonable, the local density approximation, (LDA), gives notably correct results, even for systems for which this approximation does not seem to be valid. One of the fundamental reasons for this good performance is that the large kinetic energy is treated exactly^[29,64]. This accuracy, beside the fact that the DFT transforms the many-body problem to a one-particle problem, is the major attractiveness of the theory.

In contrast to the Hartree-Fock picture, which begins conceptually with a definition of individual electrons interacting with the nuclei and all other electrons in the system, DFT starts with a consideration of the entire electron system. In DFT, the total electron density is decomposed into one-electron densities, which are constructed from one-electron wave functions^[33-35].

DFT has been successfully extended to open-shell systems and magnetic solids^[37-38]. In these cases, the local exchange-correlation energy depends not only on the local electron density, but also on the local spin density (if the densities of spin-up and spin-down electrons are not same, LDA changes to the local spin density approximation (LSDA)). LSDA treats the densities of spin-up and spin-down electrons separately.

It is not clear which of the two pictures, the Hartree-Fock approach or the local density functional approach gives better results. Actually, the applicability of the Hartree-Fock picture versus the local density approximation depends on the effective range of many-body interactions between electrons. If these interactions are of dimensions of several interatomic distances, then the Hartree-Fock approximation is better. If, however, these many-body effects are of a more short-range nature, then the local density approximation is more appropriate. Experience shows that for many systems, the LDA gives surprisingly good results, especially for the prediction of structural properties. This may be taken as evidence of the more local character of many-body interactions for many systems of interest^[29, 64, 33-35, 71].

DFT, originally intended for metallic solid-state systems, turned out to be also surprisingly successful for describing the structure and energetics of molecules. First clear evidence for the capabilities of the local density functional approach for molecular systems was given already in the 1970's, but only recent systematic calculations on a large number of typical molecules together with the introduction of gradient corrected density functionals (like Becke's (B88)). Lastly, hybrid methods became popular which they use of a mixture of Hartree-Fock exchange and DFT exchange. In this new method, the exchange-correlation energy term is corrected and calculated by the help of the exact exchange at the Hartree-Fock level ^[34,52]. Becke's three parameter is hybrid functional. The combination of Becke's three parameter gradient corrected hybrid functional and the LYP (developed by Lee, Yang, and Parr) is very popular. ^[34].

2.3 Fundamental Problems in DFT

DFT offers a powerful and excellent method for calculating the ground-state total energy and electron density of a system of interacting electrons. The whole theory is based on functionals of the electron density, which therefore plays the central role. However, the key functional, which describes the total energy of the electrons as a functional of their density, is not known exactly: the part of it that describes electronic exchange and correlation has to be approximated in practical calculations.

In 1986, Michael Schlüter, Lu Sham and R. W. Godby ^[42, 43] calculated an accurate exchange-correlation potential for silicon using many-body perturbation theory, and they showed the "band-gap problem", the observation that the electronic band gap of semiconductors in DFT calculations was only about half of the experimental band gap. They concluded that the band gap problem was inherent in DFT and not due to the approximations used in the various functionals.

Due to poor description of unoccupied orbital energy levels in Hartree-Fock approximation, the band gap values are overestimated by several electron volts in low band gap polymers ^[47]. On the other hand, DFT based methods tend to systematically underestimate the band gaps of low band gap polymers ^[47-48].

However, recent developments of DFT/hybrid functionals that include a weighted contribution of Hartree-Fock and DFT exchange allow a better evaluation in the band gap results ^[44,47]. In order to improve the calculated band gap values, Salzner et al. ^[45] for instance, studied DFT/hybrid approach and they come to the conclusion that the best extrapolated band gaps of polymers are obtained with hybrid functionals containing 30% of Hartree-Fock exchange in combination with the P86 correlation functional. Since exact exchange tends to reduce the self-interaction, the band gaps are corrected in the direction of larger band gaps, which was the desired effect in the case of the work of Salzner et al. ^[45]

Chapter 3. Methods

In our study, all calculations were performed with *Gaussian 98* ^[49] Windows and UNIX versions and for all calculations DFT was used. Energy levels of homo oligomers of ThP, F-ThP, Qx and co-oligomers of these structures with thiophene and pyrrole were optimised in planar geometry and with *trans* oriented units. Origin 7.0 program is used to sketch the graphs. The calculations were carried out using the CEP-31G* basis set with B3P86-30% functional. (Weight of the Hartree-Fock exchange was increased to 30% because a functional yields HOMO-LUMO gaps in close agreement with λ_{max} values from UV spectroscopy). Polymer properties for band gaps and band widths were evaluated by plotting results for oligomers with increasing chain length against $1/n$, (n is the number of repeat units). The data were extrapolated using second-order polynomial fits. Extrapolating energy levels were calculated for monomers through octamers for ThP, monomers through tetramers for F-ThP and Qx for homopolymers to infinity. For ThP-Th, and ThP-Py co-oligomers, extrapolating energy levels were calculated monomers through tetramer and, for F-ThP-Py monomers through trimer data were used. IPs and EAs are taken as negative HOMO and LUMO energies.

Chapter 4. Results and Discussion

4.1 Homopolymers

4.1.1 Poly(thieno [3,4-b] pyrazine), PThP

Oligomers, from monomer to tetramer, hexamer, and octamer were investigated in aromatic (end-capped with hydrogen) and quinoid (end-capped CH₂) groups.

a) Geometries:

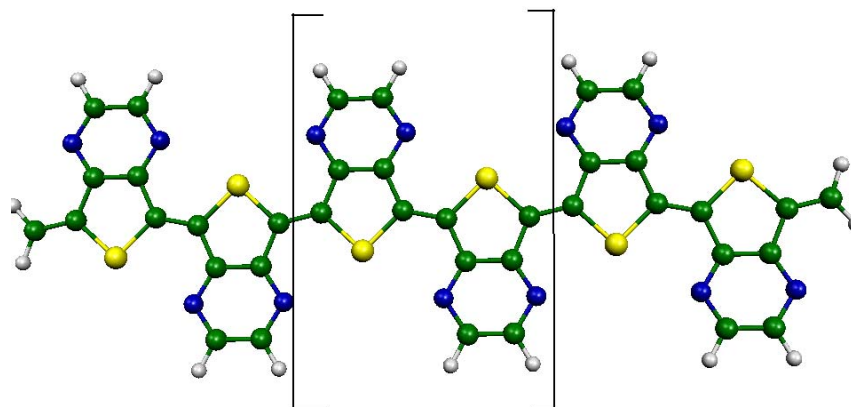
In order to determine the geometric preferences, whether the ground state of oligomers is quinoid or aromatic, I calculated the energies of aromatic and quinoid forms of structures. CH₂ groups at the terminal carbon atoms force the outermost rings to be quinoid, inclining the whole system towards a quinoid form. In contrast, hydrogen atoms at the terminal position have opposite effect by forcing the terminal ring to be aromatic.

To determine the energy difference between quinoid and aromatic form of ThP, we calculated the energy of the innermost units in quinoid and aromatic arrangements and subtracted energies of oligomers having repeat unit of n, and (n-2) (table 4.1.1). In this way the effects of end groups are removed and the energy of the inner rings remains. Thus, this calculation allows us to determine which geometry is more stable (Table 4.1.1).

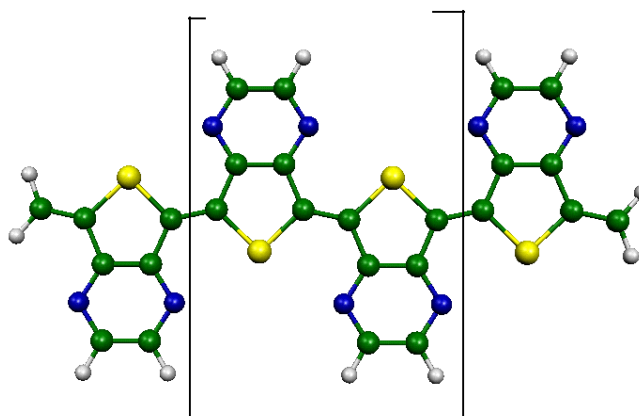
n-(n-2) , n: repeat unit	ΔE (kcal/mol)	stable system
tetramer-dimer	5.46	Quinoid
hexamer -tetramer	4.71	Quinoid
octamer-hexamer	4.42	Quinoid

Table 4.1.1 Energy difference in aromatic and quinoid type of structures per two rings

Below picture is an example for above calculations:

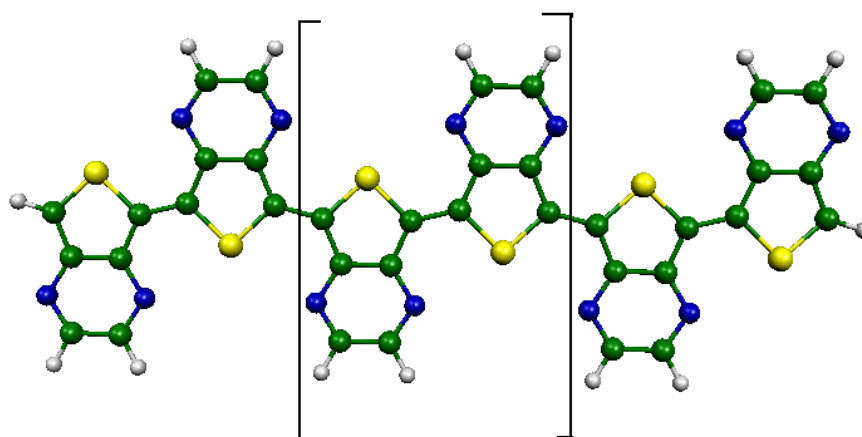


(a)

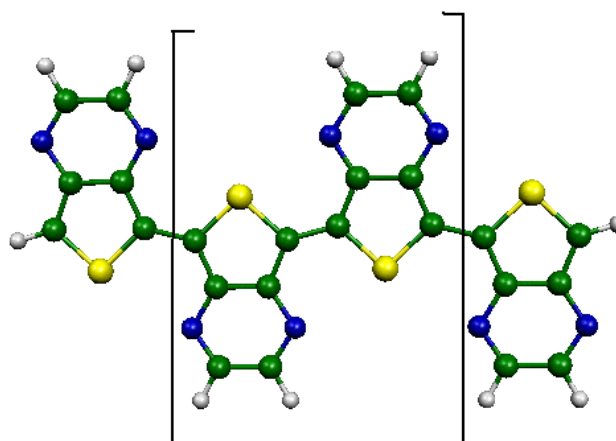


(b)

Figure 4.1.1 Quinoid forms of hexamer (a) and tetramer (b) of Thieno [3,4-b] pyrazine



(a)



(b)

Figure 4.1.2 Aromatic forms of hexamer (a) and tetramer (b) of Thieno [3,4-b] pyrazine

We compared the energies of inner two rings to understand whether they prefer aromatic or quinoid form in the ground state (Table 4.1.2).

Energy (kcal/mol)	Aromatic form (kcal/mol)	Quinoid form (kcal/mol)
$E_{n=2}$	-83729.04	-91726.95
$E_{n=4}$	-166688.45	-174691.82
ΔE_{4-2}	-82959.41	-82964.87

$$\Delta (\Delta E_{4-2}) = (5.46 \text{ kcal/mol per two ring quinoid form more stable})$$

Table 4.1.2 Ground state energies of aromatic and quinoid forms of hexamer and tetramer of Thieno [3,4-b] pyrazine

The quinoid form of ThP is more stable than the aromatic form by about 2-3 kcal/mol per ring. The preference for a quinoid structure of poly (thieno [3,4-b] pyrazine) (PThP) can also be investigated by evaluating bond length variations upon chain length increase. Especially, the change in inter-ring bond length can give an idea about the favoured structure. Upon increase of chain length, the inner part of the oligomer tends to adopt the more favourable structure of the system, regardless of the end groups. Inter-ring bond lengths for aromatic and quinoid forms of ThP shown in table 4.1.3.

Number of repeated unit	Inter-ring bond length (\AA°)
2	1.452
4	1.439
6	1.433
8	1.429

Table 4.1.3.a Inter-ring bond lengths of aromatic ThP

Number of repeated unit	Inter-ring bond length (\AA°)
2	1.378
4	1.384
6	1.386
8	1.386

Table 4.1.3.b Inter-ring bond lengths of quinoid ThP

Inter-ring bond lengths for the polymer were calculated with polynomial fit;

Polynomial fit for aromatic form : 1.417 Å

Polynomial fit for quinoid form : 1.386 Å

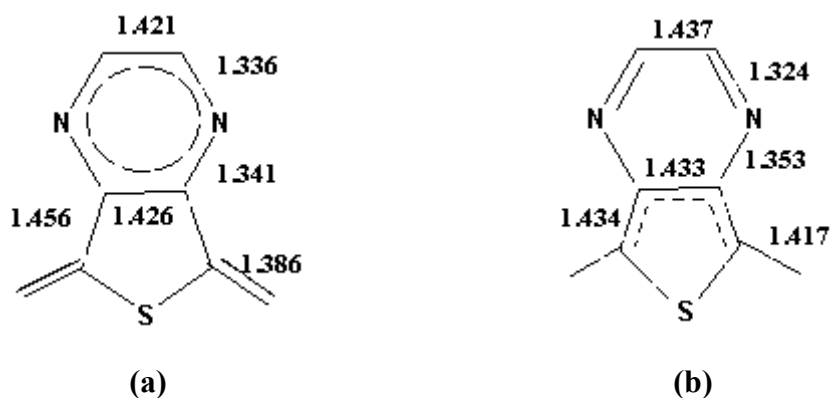


Figure 4.1.3 Geometries of the inner-ring in quinoid form of poly (thieno [3,4-b] pyrazine) (a), and aromatic form of poly (thieno [3,4-b] pyrazine) (b)

In the quinoid form the pyrazine ring has aromatic character. When the thiophene rings are aromatic, the pyrazine rings can have only two double bonds (Figure 4.1.3). The ultimate structure is thus a compromise between delocalization energies in pyrazine and thiophene.

As shown in table 4.1.3 inner-ring bond lengths of aromatic forms decrease and those of quinoid forms increase while the chain length increases. The preference for the quinoid form is confirmed by the fact that the inter-ring bond length is 1.386 Å, and that it changes little with increasing chain length. These small changes in the bond lengths between the larger oligomers show that the geometries of the inner rings of the hexamer have converged to the polymer values. In contrast, in the aromatic form the inter-ring bond length decreases significantly with increasing chain length, as the inner rings are trying to switch to the quinoid conformation. However even for the octamer, the inner rings of the aromatic form have not switched completely to a quinoid structure.

For quinoid forms, the effect of terminal -CH₂ groups on the inner-ring bond lengths decrease while the chain length increases. The calculations support this idea.

The bond length alternation of poly (thieno [3,4-b] pyrazine) is 0.07 Å.

The estimated inter-ring bond length based on Badger's rule is 1.42 Å, indicating that the average structure is about 30% quinoid like. (L. Cuff and M. Kertesz determined bond distances ^[50] through the application of Badger's rule). Accordingly,

$$F^{-1/3} = ar + b \quad (\text{Equation 4.1.1})$$

where F is the stretching force constant in mdyn/Å, r is the C-C bond length in Å, and a and b are constants.

The inner- ring bond distance for ThP was found as 1.39 Å, this is shorter than estimated value.

b) Band Gaps and Band Widths:

Table 4.1.4 summarizes the IPs and EAs of ThP oligomers with increasing chain length. I showed HOMO-LUMO gap change with increasing number of repeat units for ThP in Figure 4.1.4.

n, rep. unit	IPs (eV)	EAs (eV)	E _g (eV)
1	6.8	2.4	4.4
2	6.2	2.9	3.3
3	5.9	3.1	2.8
4	5.7	3.3	2.4
∞	5.2	3.8	1.4

Table 4.1.4 IPs, EAs and E_g for quinoid forms of ThP oligomers and for PThP

IPs and EAs of all oligomers are plotted against to $1/n$ (number of repeating units), and polymeric IPs and EAs are obtained by extrapolation. The results with four and six data points differ by less than the overall accuracy. For six data points IP (5.2 eV) and EA (3.8 eV) these data are same with four data points and thus I used four data points for the other systems.

All points on the curves are fitted according to second order polynomial fitting, since correlation is improved with polynomial fitting compared to linear fitting, and correlation coefficients of these curves are found to be 0.99 or larger.

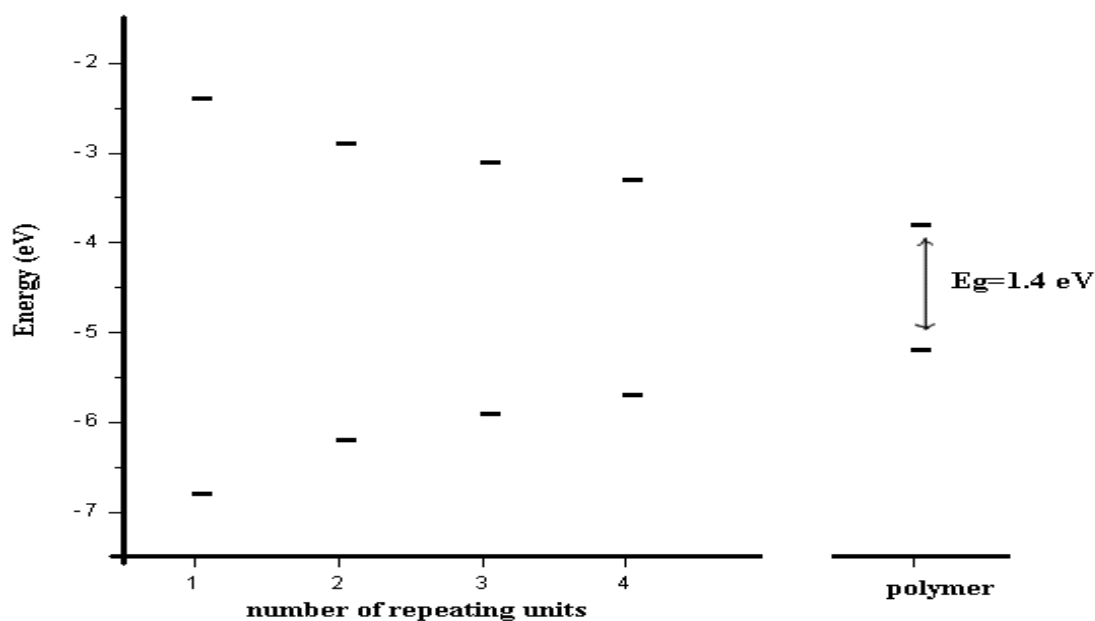


Figure 4.1.4 HOMO-LUMO gap change with increasing number of repeat units for quinoid forms of thieno [3,4-b] pyrazine (ThP)

The band gap of PThP is 1.4 eV. Experimental (electrochemical) band gap value for PThP is close to 1 eV [9, 72, 73]. Experimental band gaps are the onset of absorption of a solid. According to the Franck-Condon principle, the highest intensity (λ_{\max}) in absorption spectra corresponds to a vertical excitation since the electronic excitation is fast with respect to nuclear relaxation. For polyenes and aromatic heterocycles, the lowest allowed excitations are singlet $\pi \rightarrow \pi^*$ transitions. Therefore, theoretical energy gaps are λ_{\max} values of individual molecules [45]. There is about 0.5 eV difference between theoretical λ_{\max} values calculated for isolated chains and condensed phase band gap values. After correcting, our theoretical band gap values agree with experimental results.

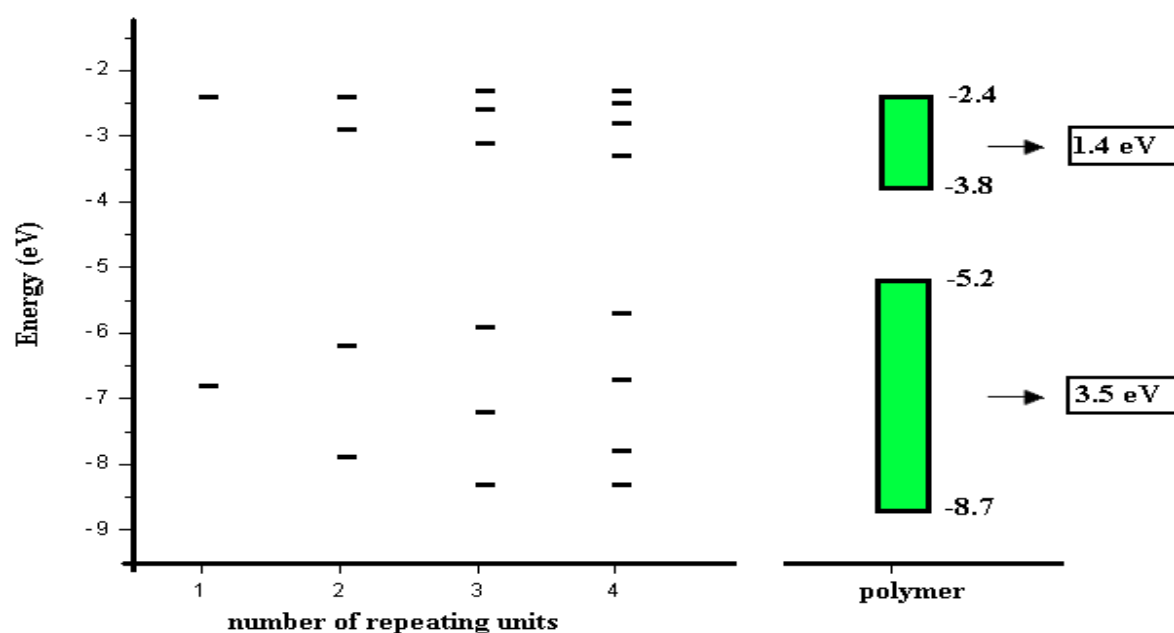


Figure 4.1.5 Development of the band structure of poly (thieno [3,4-b] pyrazine) from energy levels of oligomers of thieno [3,4-b] pyrazine (quinoid forms)- (Monomer is used as repeat unit)

The band widths of valence and conduction band of PThP are 3.5 eV and 1.4 eV, respectively (Figure 4.1.5). The width of the bands depends on the strength of the interaction between the repeat units. Weak interaction leads to little delocalisation, narrow bands, and poor mobility.

4.1.2 Fluorine- Substituted Poly(thieno [3,4-b]pyrazine), F-PThP

a) Geometries:

We increased the acceptor power of thieno [3,4-b] pyrazine by adding fluorine atoms, however there are little changes in the geometries (Figure 4.1.6)



Figure 4.1.6 Geometries of inner rings of PThP and F-PThP

To determine the geometric preferences, aromatic or quinoid, we made similar calculations as we showed for PThP. The quinoid form of F-PThP is about 3 kcal/mol per ring more stable than the aromatic form. This is consistent with geometrical results. The structure of F-PThP is quinoid if the inter-ring bond length of 1.383 Å is taken as a criterion.

The bond length alternation of fluorine-substituted poly (thieno [3,4-b] pyrazine) is 0.071 Å.

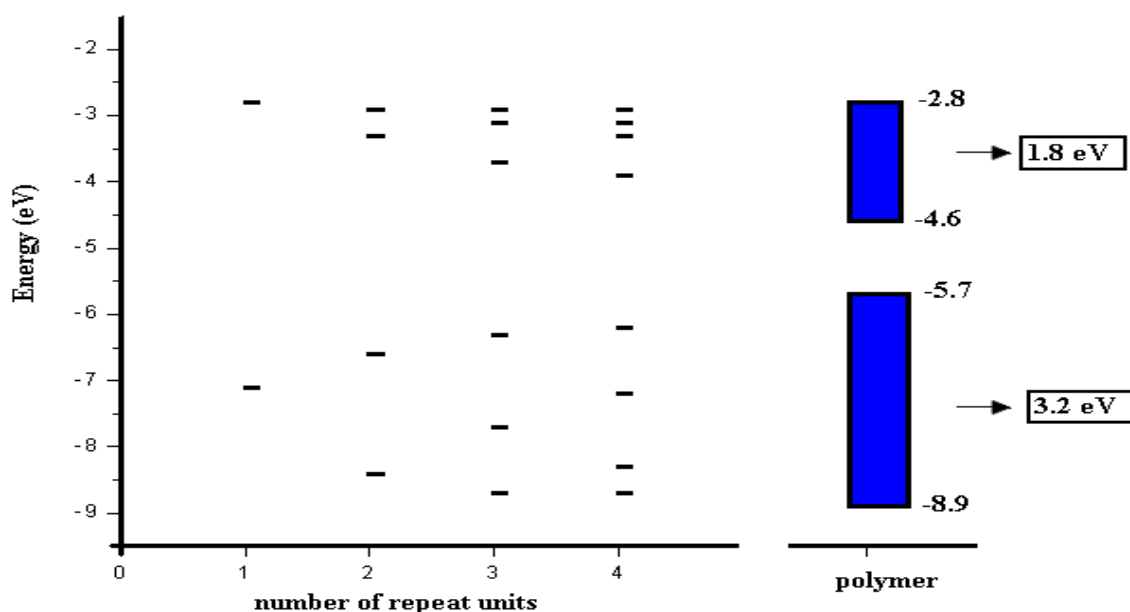
b) Band Gaps and Band Widths:

Table 4.1.5 summarizes the IPs, EAs, and E_g values of F-PThP. With adding fluorine groups to ThP, IP value changes from 5.2 eV to 5.7 eV and EA changes from 3.8 eV to 4.6 eV. Thus for F-PThP band gap is smaller (1.1 eV) than PThP (1.4 eV).

n, rep. unit	IPs (eV)	EAs (eV)	E _g (eV)
1	7.1	2.8	4.3
2	6.6	3.3	3.3
3	6.3	3.7	2.6
4	6.2	3.9	2.3
∞	5.7	4.6	1.1

Table 4.1.5 IPs, EAs, and band gaps of F-PThP

F-PThP has a wider conduction band (1.8 eV) and a narrower valence band (3.2 eV) than hydrogen substituted ThP. (These values are 1.4 eV and 3.5 eV in the hydrogen substituted ThP homopolymer case).

**Figure 4.1.7** Development of the band structure of F-PThP from energy levels of oligomers of fluorine substituted thieno [3,4-b] pyrazine. (Monomer is used as repeat unit).

4.1.3 Polyquinoxaline, PQx

a) Geometries:

The aromatic form of polyquinoxaline, PQx is about 10 kcal/mol more stable than the quinoid form. Accordingly the inner-ring bond length is 1.515 Å. Figure 4.1.8 shows the geometry of the inner ring of PQx. The bond length alternation of polyquinoxaline is 0.05 Å.

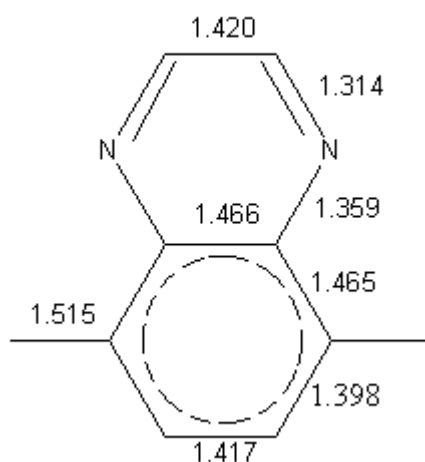


Figure 4.1.8 Geometries of inner rings of Quinoxaline

b) Band Gaps and Band Widths:

In table 4.1.6 IPs and EAs are summarized for oligomers of polyquinoxaline.

n, rep. unit	IPs (eV)	EAs (eV)	E _g (eV)
1	7.8	2.4	5.4
2	7.0	2.8	4.2
3	6.7	3.0	3.7
4	6.5	3.1	3.4
∞	5.9	3.5	2.4

Table 4.1.6 IPs, EAs, and band gaps of PQx

The band gap of PQx is 2.4 eV. The band widths of valence and conduction band of PQx are 2.0 eV and 1.6 eV, respectively (Figure 4.1.9).

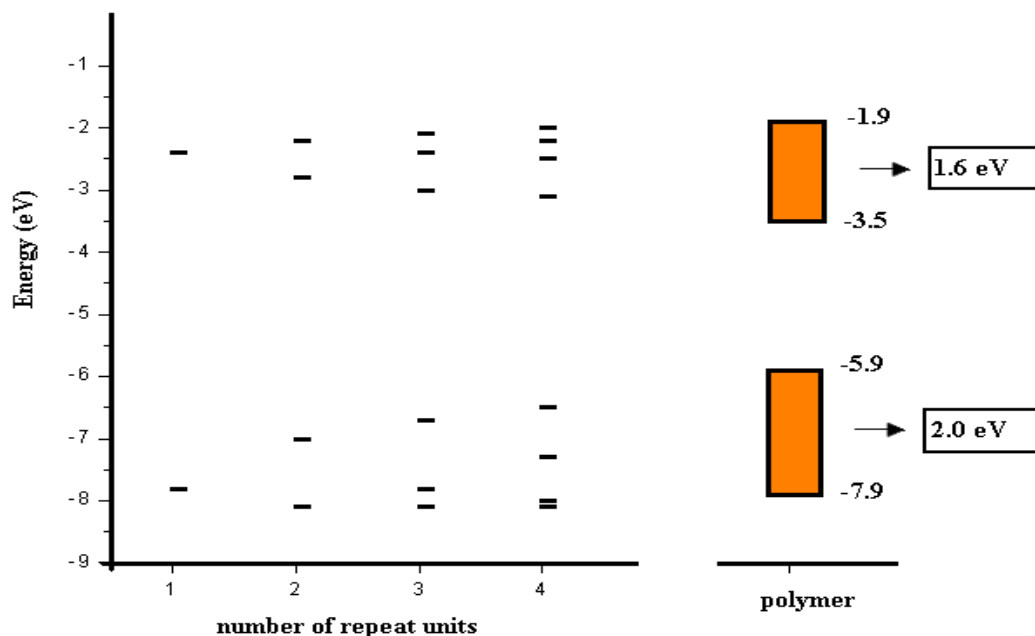


Figure 4.1.9 Development of the band structure of poly (quinoxaline) from energy levels of oligomers of quinoxaline

4.1.4 Comparison of IPs, EAs, Band Widths, and Band Gaps of Homopolymers

Table 4.1.7 summarizes the IP, EA, Eg, valence and conduction band width values of PThP, F-PThP, and PQx. The F-ThP has smaller band gap. PQx has larger band gap and relatively smaller band width values. We increased the acceptor power of PThP by adding fluorine units. Due to energy levels, F-PThP is the better acceptor. Band gap is decreased about 0.3 eV, with adding fluorine, however, valence band width decreased, too. In figure 4.1.10, energy levels, band gaps, and band widths shown clearly.

polymer	IP (eV)	EA (eV)	E_g (eV)	Valence band width (eV)	Conduction band width (eV)
PThP	5.2	3.8	1.4	3.5	1.4
F-PThP	5.7	4.6	1.1	3.2	1.8
PQx	5.9	3.5	2.4	2.0	1.6

Table 4.1.7 IPs, EAs, band gaps, valence and conduction band width values as eV of PThP, F-PThP, and PQx

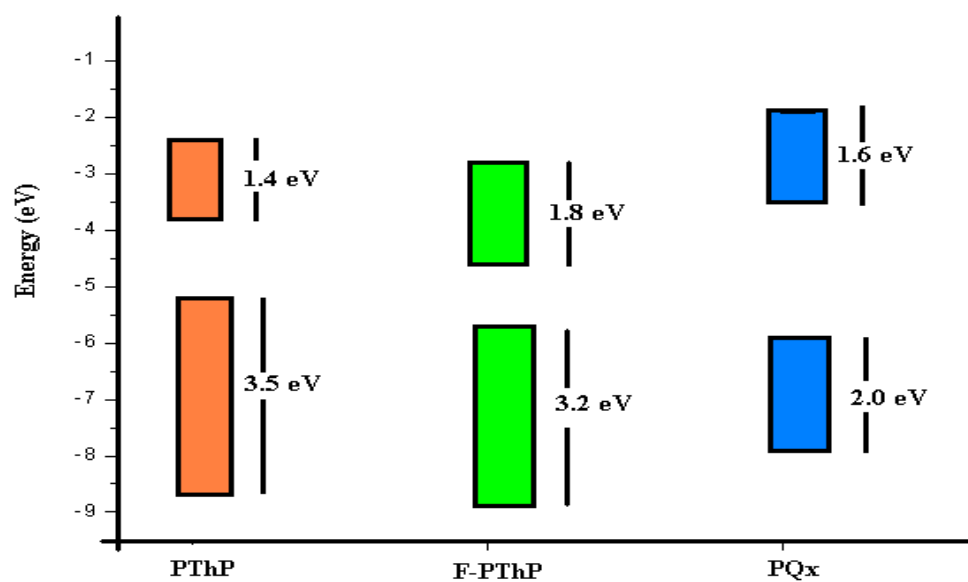


Figure 4.1.10 Schematic representation of energy levels, band gaps and band widths of homopolymers

4.2 Copolymers

4.2.1 1:1 Donor/Acceptor Ratio Copolymers

4.2.1.1 Poly [(thieno [3,4-b] pyrazine)-thiophene], P(ThP-Th)

Co-oligomers of ThP and Th units are shown in Figure 1.6.4. In order to determine whether the ground state of P(ThP-Th) is quinoid or aromatic, energy difference between co-oligomers having repeat unit of n , and $(n-2)$ are calculated individually for quinoid and aromatic forms of systems.

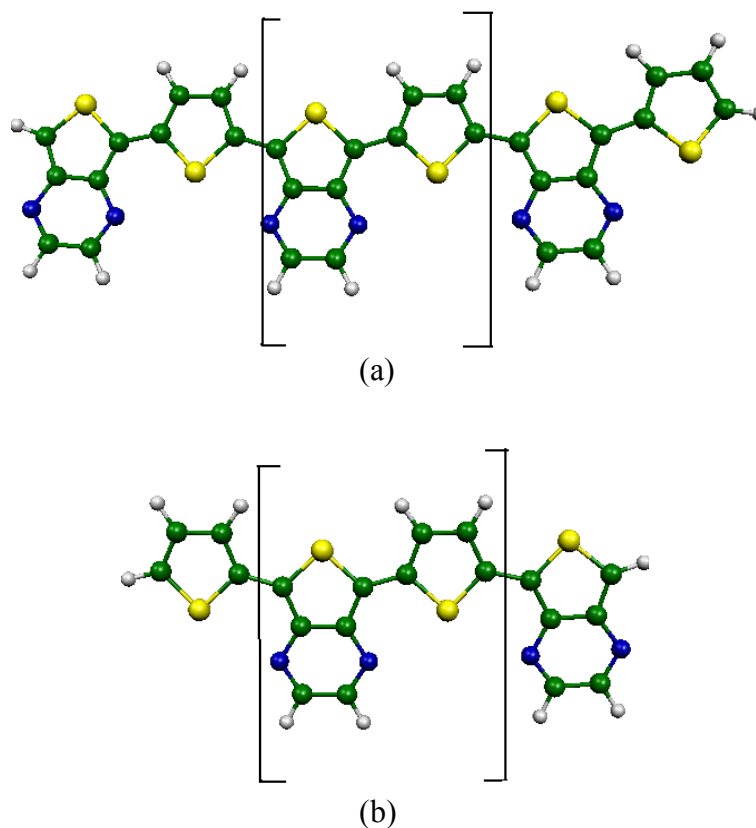


Figure 4.2.1 Aromatic forms of trimer (a) and dimer (b) of 1:1 donor-acceptor ratio of (thieno [3,4-b] pyrazine -thiophene) co-oligomers

We compared the energies of the inner rings to understand whether they prefer aromatic or quinoid form in the ground state. Calculations show that the aromatic form of poly (ThP-Th) is ~2 kcal/mole per unit more stable than the quinoid form.

Th oligomers are more stable in the aromatic form by about 6 kcal/mol per ring. [9, 74]. Considering that ground state of PThP has a 2-3 kcal/mol more stable quinoid structure, aromatic preferences of copolymer seems plausible.

Since Th prefers aromatic structures and ThP prefers quinoid structures, a geometric mismatch results upon copolymerisation. Calculations have been made up to four member aromatic and quinoid structures.

a) Geometries:

Inter-ring bond lengths for aromatic and quinoid forms of (thieno [3,4-b] pyrazine -thiophene) co-oligomers shown in table 4.2.1

no. of repeated unit	Inter-ring bond length (\AA°)
1	1.460
2	1.450
3	1.448
4	1.447

i) aromatic

no. of repeated unit	Inter-ring bond length (\AA°)
1	1.380
2	1.389
3	1.392
4	1.394

ii) quinoid

Table 4.2.1 Inter-ring bond length variation in aromatic and quinoid forms of ThP-Th co-oligomers

The ThP-Th co-oligomer has longer inter-ring bond length (1.447 \AA) than the ThP homo oligomer (1.386 \AA), however, it has shorter inter-ring bond length than Th (1.459 \AA). Bond lengths of ThP-Th co-oligomers are between bond lengths of homo oligomers ThP and Th. (Figure 4.2.2). The copolymer has less bond length alternation (0.033 \AA) than in either homopolymer. (Bond length alternation values are 0.07 \AA for PThP and 0.063 \AA for PTh).

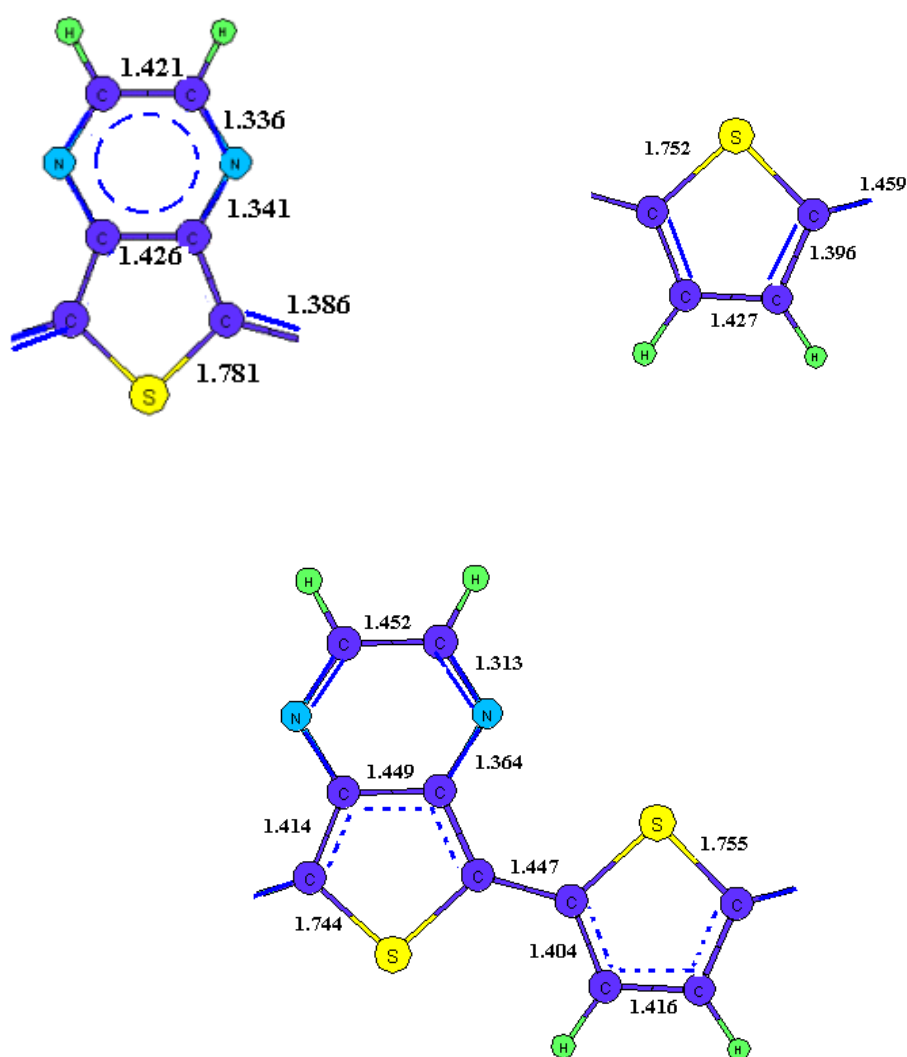


Figure 4.2.2 Optimized structures of inner rings of homopolymers PTh (a), and PThP (b) and copolymer P(ThP-Th) (c)

Structures of the thiophene rings are distorted compared to those in the homopolymers. In the thieno pyrazine fragment, the thiophene ring has switched to the aromatic structure.

b) Band Gaps and Band Widths:

In table 4.2.2 HOMO and LUMO energy levels are summarized for co-oligomers of (ThP-Th).

n, rep. unit	IPs (eV)	EAs (eV)	E _g (eV)
1	6.5	3.0	3.5
2	5.9	3.3	2.6
3	5.6	3.5	2.1
4	5.5	3.6	1.9
∞	5.1	3.9	1.2

Table 4.2.2 IPs, EAs, and band gaps of P(ThP-Th)

Band gap of P(ThP-Th) is 1.2 eV. The band widths of valence and conduction bands of P (ThP-Th) are 2.6 eV and 1.1 eV, respectively (Figure 4.2.3).

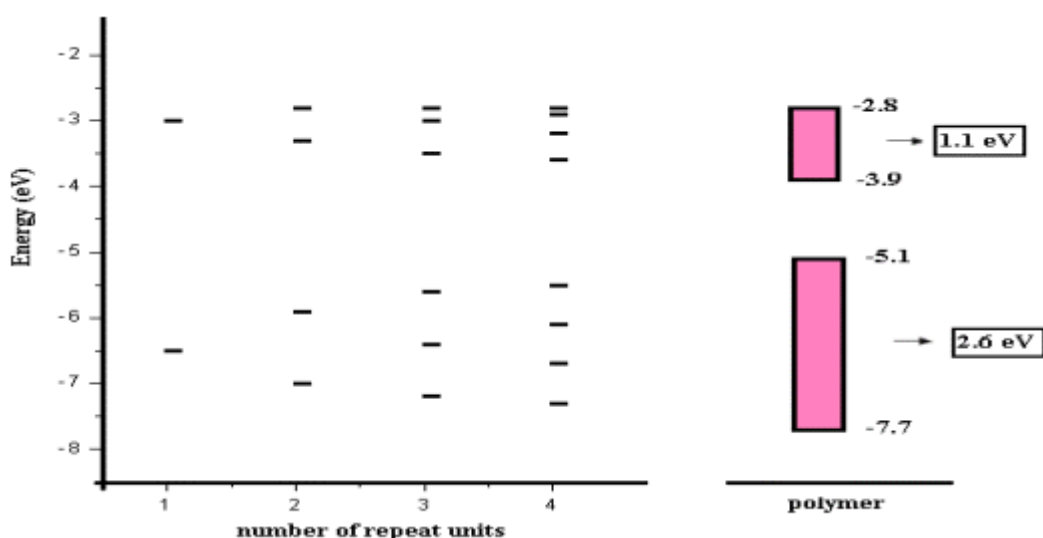


Figure 4.2.3 Development of the band structure of poly (ThP-Th) from energy levels of co- oligomers of (thieno [3,4-b] pyrazine- thiophene)

In order to make a comparison between band gaps and band widths of homopolymers and copolymers, we must have same number size of repeating units. Thus, I handled PThP homo oligomers up to octamer, and for comparing band widths and band gaps with poly (ThP-Th), I used dimer as repeat unit.

Figure 4.2.4 shows the HOMO-LUMO difference of ThP oligomers and band gap of PThP, when dimer is used as the repeat unit. The band gap is 1.4 eV and the widths of valence and conduction bands are 2.3 eV and 1.1 eV, respectively.

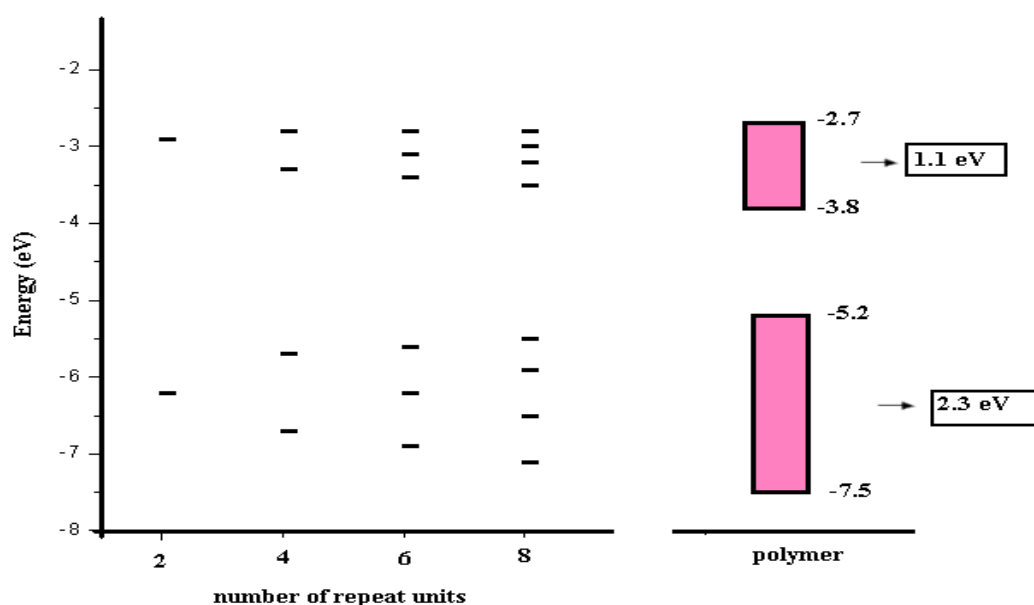


Figure 4.2.4 Development of the band structure of PThP from energy levels of oligomers of ThP. (Dimer is used as repeat unit).

According to the donor-acceptor concept, we should predict smaller band gap and wider bands than homopolymers. Band gaps are 2.2 and 1.4 eV for PTh and PThP homopolymers. Band gap is decreased to 1.2 eV the copolymer. So, there is a significant decrease of the band gap. Valence band of P(ThP-Th) is 0.3 eV wider than of both PThP and PTh but it has same size of conduction band with PThP. Moreover, the conduction band width of PTh, 0.9 eV is larger than that of the copolymer.

4.2.1.2 Poly[(thieno [3,4-b]pyrazine)-pyrrole] , P(ThP-Py)

For copolymers of ThP with pyrrole (Py), we found the aromatic structure to be preferred by about 3 kcal/mol.

a) Geometries:

Inter-ring bond lengths for aromatic and quinoid forms of (thieno [3,4-b] pyrazine -pyrrole) co-oligomers shown in table 4.2.3.

no. of repeated unit	Inter-ring bond length (Å ^o)	no. of repeated unit	Inter-ring bond length (Å ^o)
1	1.454	1	1.386
2	1.447	2	1.395
3	1.445	3	1.401
4	1.445	4	1.403

i) aromatic

ii) quinoid

Table 4.2.3 Inter-ring bond length variation in aromatic and quinoid forms of ThP-Py co-oligomers

The copolymer of ThP with Py does not show a significant difference in geometric properties compared to copolymers of ThP with Th. Bond length alternation is 0.033 Å^o. (Figure 4.2.5).

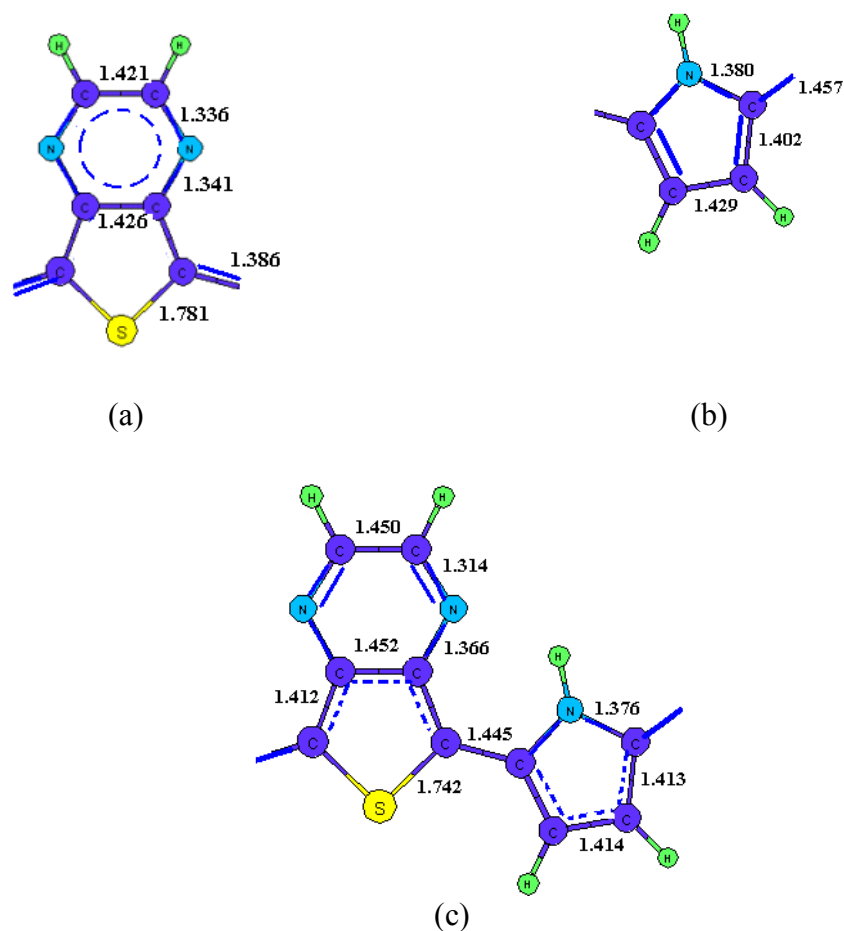


Figure 4.2.5 Optimized structures of inner rings of homopolymers; PThP (a) and polypyrrole (PPy) (b), and copolymer P (ThP-Py) (c)

b) Band Gaps and Band Widths:

In table 4.2.4 HOMO and LUMO energy levels are summarized for co-oligomers of (ThP-Py).

n, rep. unit	IPs (eV)	EAs (eV)	E _g (eV)
1	6.1	2.9	3.2
2	5.5	3.2	2.3
3	5.3	3.3	2.0
4	5.2	3.3	1.9
∞	4.8	3.6	1.2

Table 4.2.4 IPs, EAs, and band gaps of P(ThP-Py)

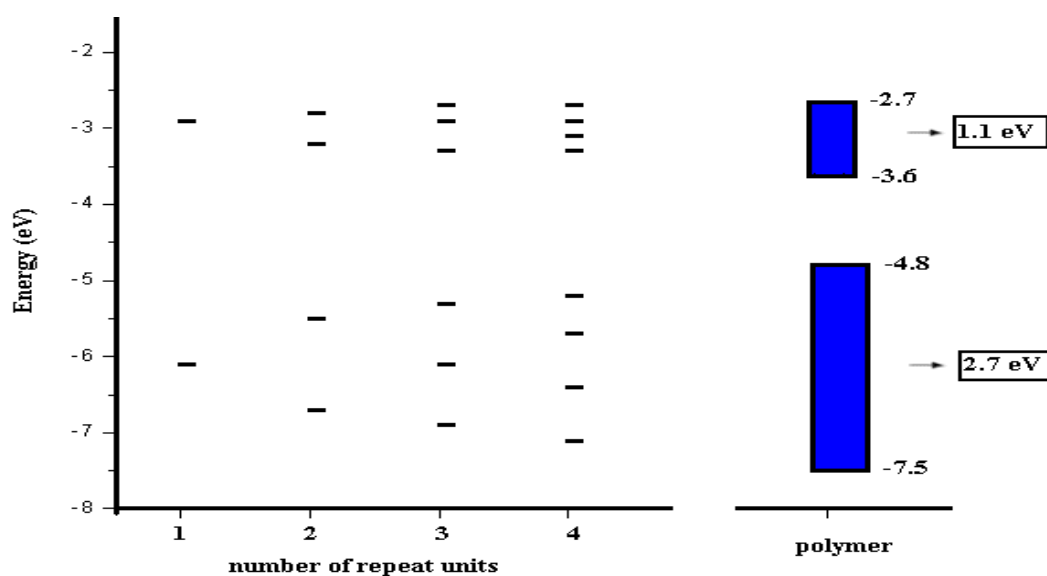


Figure 4.2.6 Development of the band structure of poly (ThP-Py) from energy levels of co- oligomers of (thieno [3,4-b] pyrazine- Pyrrole). (Dimer is used as repeat unit).

P(ThP-Py) has the same band gap (1.2 eV) as P(ThP-Th.). Also, P(ThP-Py) has the same conduction band width (1.1 eV) as P(ThP-Th) and it has a slightly wider valence band (2.7 eV) than P(ThP-Th) (2.6 eV). (Figure 4.2.6). Thus, the stronger donor, pyrrole does not lead to a smaller band gap and wider bands than the weaker donor thiophene. This is in qualitative and quantitative contradiction with the donor-acceptor concept.

4.2.1.3 Fluorine Substituted Copolymers: Poly [(thieno [3,4-b] pyrazine)-thiophene], P(F-ThP-Th) and Poly [(thieno [3,4-b]pyrazine)-pyrrole], P(F-ThP-Py)

a) Geometries:

Additions of Fluorine groups to the acceptor parts of co-oligomers do not change geometries very much. (Figure 4.2.7).

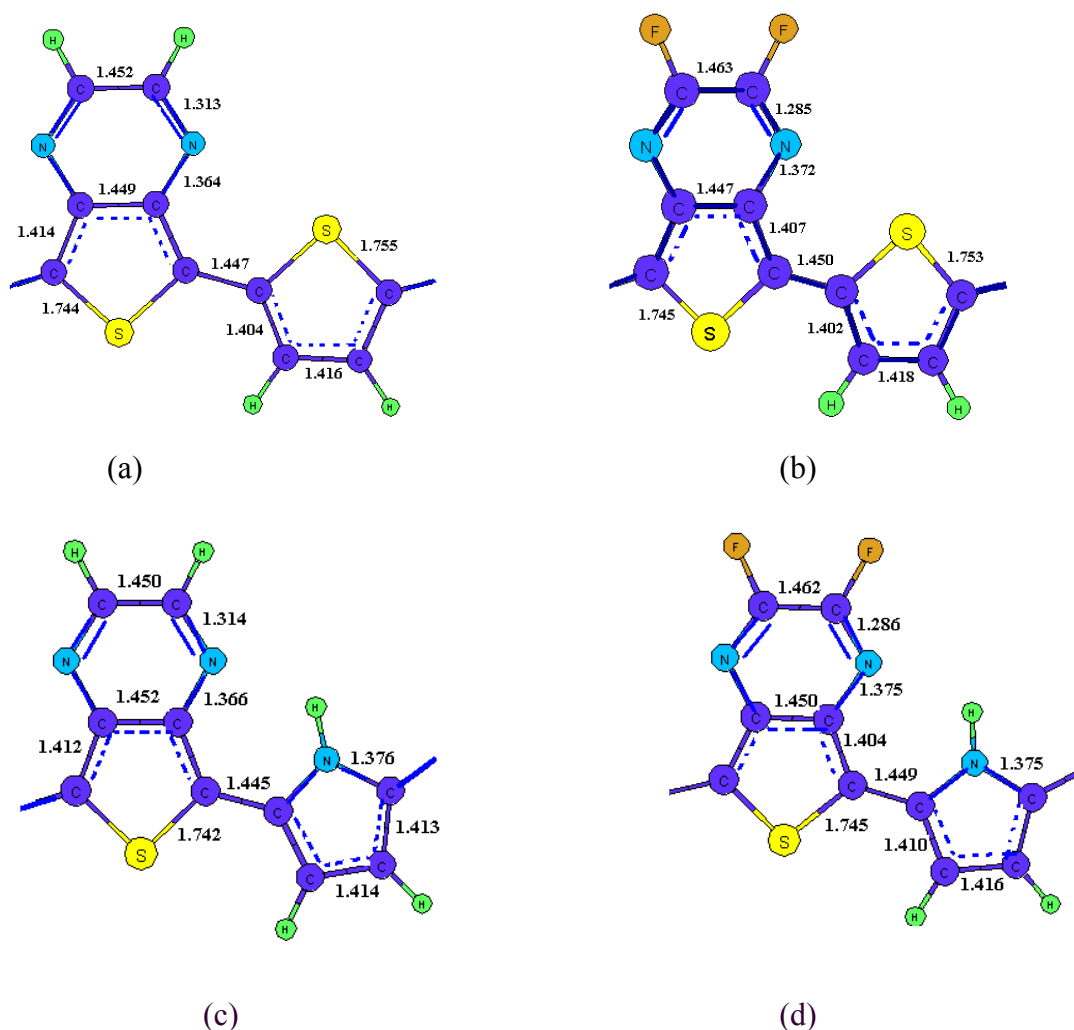


Figure 4.2.7 Geometries of inner rings of P(ThP-Th) (a), P(F-ThP-Th) (b), P(ThP-Py) (c), and P(F-ThP-Py) (d)

Bond length alternations for P(F-ThP-Th) and for P(F-ThP-Py) are 0.043 Å and 0.045 Å, respectively.

b) Band Gaps and Band Widths:

Table 4.2.5 summarizes the IPs, EAs and band gaps of Fluorine substituted ThP-Th co-oligomers with increasing chain length.

n, rep. unit	IP (eV)	EA (eV)	E _g (eV)
1	6.8	3.2	3.6
2	6.2	3.6	2.6
3	6.0	3.8	2.2
∞	5.6	4.2	1.4

Table 4.2.5 IPs, EAs and E_g values for Fluorine substituted ThP-Th co-oligomers

Fluorine substituted ThP-Th co-oligomer has a larger band gap (1.4 eV) than the hydrogen substituted ThP-Th co-oligomer (1.2 eV). Valence and conduction bands for P(F-ThP-Th) are 2.5 eV and 1.2 eV, respectively. When fluorine units are added to the co-oligomer, the conduction band width increased about 0.1 eV, however, the valence band width decreased by the same amount. Thus, increasing the acceptor strength does not decrease the band gap as predicted by the donor-acceptor concept.

4.2.1.4 Copolymers of Quinoxaline with Thiophene P(Qx-Th), and Pyrrole P(Qx-Py)

a) Geometries:

Figure 4.2.8 summarizes the inner ring bond length changes when quinoxaline forms co-oligomers with thiophene and pyrrole. Bond length alternations for Qx-Th and for Qx-Py are 0.033 Å and 0.024 Å, respectively.

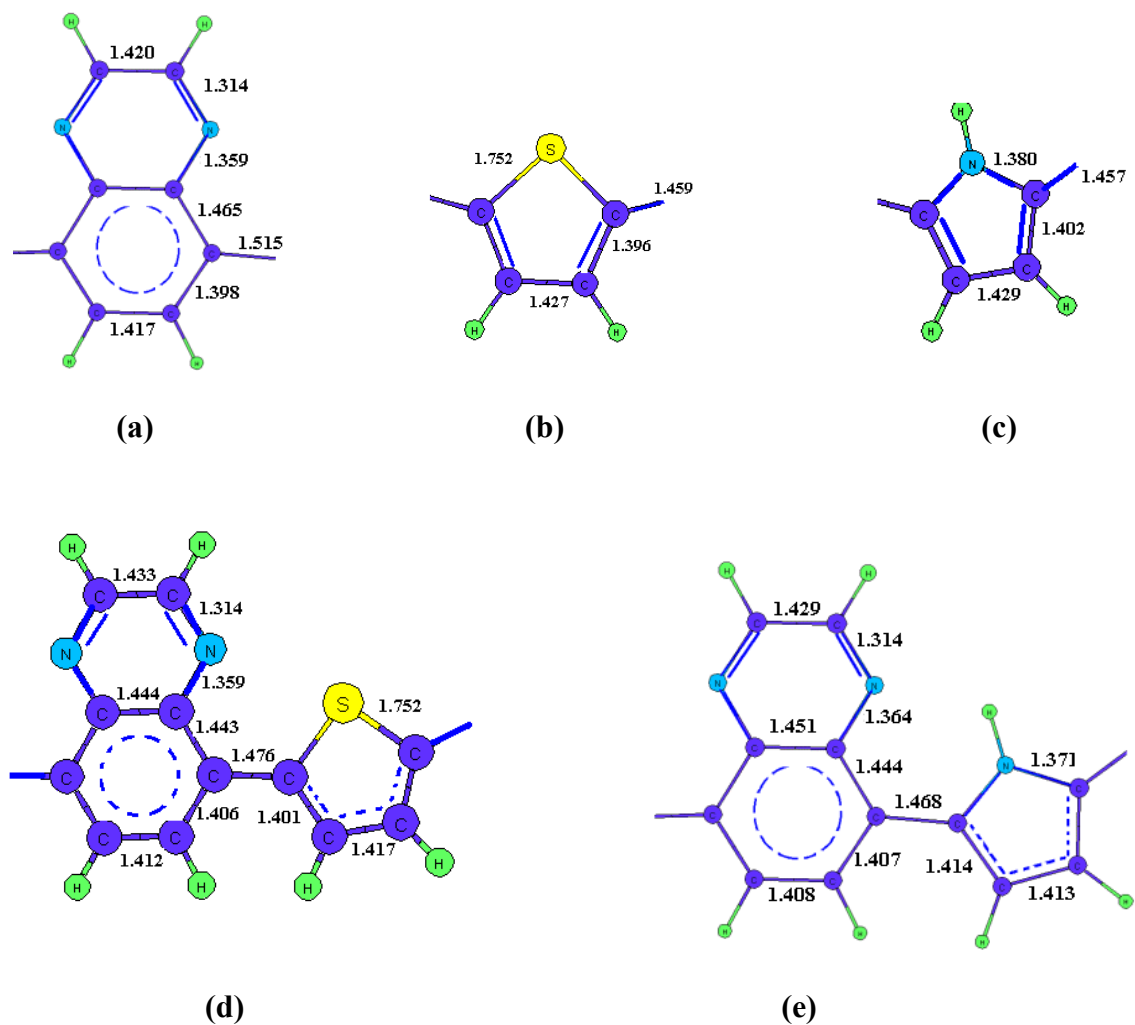


Figure 4.2.8 Optimized structures of inner rings of homo oligomers; Qx (a), Th (b), Py (c), and co-oligomers Qx-Th (d), Qx-Py (e)

b) IPs, EAs, and Band Gaps:

Both of Qx-Th, and Qx-Py co-oligomers have larger band gaps than co-oligomers of ThP with Th and Py, however, quinoxaline co-oligomers have lower IP and EA values (Table 4.2.6)

n, rep. unit	IP (eV)	EA (eV)	E_g (eV)
1	6.7	2.6	4.1
2	6.1	3.0	3.1

(i)

n, rep. unit	IP (eV)	EA (eV)	E_g (eV)
1	6.2	2.6	3.6
2	5.7	2.9	2.6
3	5.5	3.0	2.5
∞	5.0	3.2	1.8

(ii)

Table 4.2.6 IPs, EAs and E_g values for Qx-Th (i) and Qx-Py (ii) co-oligomers

The P(Qx-Py) copolymer has a 1.8 eV band gap. [UV-VIS spectral data: λ_{max} =421 nm (2.95 eV) for monomer, and λ_{max} =535 nm (2.32eV) for dimer]^[53].

The P(Qx-Py) copolymer has 2.3 eV and 0.8 eV valence and conduction band width, respectively.

4.2.2 2:1 Donor/Acceptor Ratio Copolymers

4.2.2.1 Poly [thiophene-(thieno [3,4-b]pyrazine)-thiophene] , P(Th-ThP-Th)

a) Geometries:

The inner-ring bond lengths do not change when donor ratio increased from one to two in the copolymers of thieno [3,4-b] pyrazine with thiophene (Figure 4.2.9). Bond length alternation is 0.036 Å.

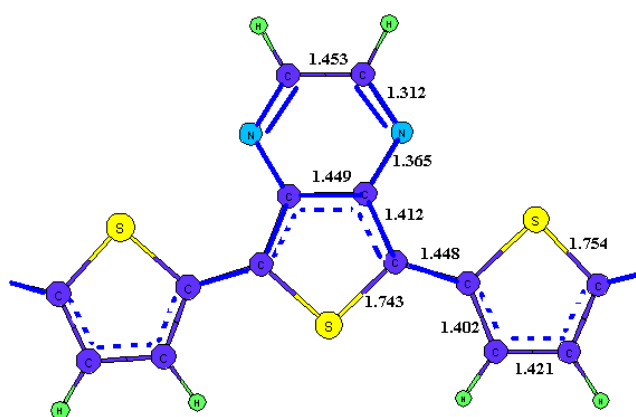


Figure 4.2.9 Optimized structures of inner rings of (Th-ThP-Th) co-oligomer

b) IPs, EAs, and Band Gaps:

Table 4.2.7 summarizes the IPs, EAs and band gaps of Th-ThP-Th co-oligomers with increasing chain length.

n, rep. unit	IP (eV)	EA (eV)	E _g (eV)
1	6.1	3.1	3.6
2	5.7	3.4	2.3
3	5.6	3.5	2.1
∞	5.3	3.7	1.6

Table 4.2.7 IPs, EAs and E_g values for Th-ThP-Th co-oligomers and P(Th-ThP-Th)

When, we increase the donor ratio in the P(ThP-Th) copolymer from one to two, the HOMO energy level decreases and the LUMO energy level increases, thus the band gap increases from 1.2 eV to 1.6 eV.

Absorption maximum of the monomer corresponding to P(ThP-Th) is 529 nm (2.34 eV)^[53] and polymer has about 1.0 eV band gap^[10, 54]. Thus, there is an overestimation (after correcting about 0.1 eV) of the band gap.

4.2.2.2 Poly [pyrrole- (thieno [3,4-b] pyrazine)-pyrrole], P(Py-ThP-Py)

a) Geometries:

The inner-ring bond lengths change little when the donor ratio increases from one to two for the copolymers of ThP with Py (Figure 4.2.10). (Bond length alternation is 0.035 Å for Py-ThP-Py co-oligomers; this value was 0.033 Å for 1:1 donor-acceptor ratio of ThP-Py co-oligomers).

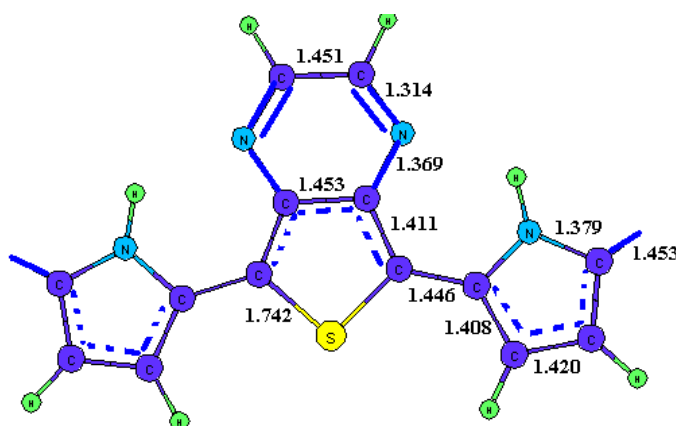


Figure 4.2.10 Optimized structures of inner rings of (Py-ThP-Py) co-oligomer

b) IPs, EAs, and Band Gaps:

Table 4.2.8 shows the IPs, EAs and band gaps of Py-ThP-Py co-oligomers with increasing chain length.

n, rep. unit	IP (eV)	EA (eV)	E _g (eV)
1	5.6	3.0	2.6
2	5.2	3.1	2.1

Table 4.2.8 IPs, EAs and E_g values for Py-ThP-Py co-oligomers

In contrast to Th-ThP-Th co-oligomers, band gaps do not increase when, we increase the donor ratio of ThP-Py co-oligomers from one to two.

The absorption maxima of the monomer corresponding to P(ThP-Py) is 616 nm (2.01 eV)^[53].

4.2.2.3 Poly [thiophene-quinoxaline-thiophene] , P(Th-Qx-Th)

a) Geometries:

Bond length alternation is 0.031 \AA for Th-Qx-Th co-oligomers; this value was 0.033 \AA for 1:1 donor-acceptor ratio of Th-Qx co-oligomers. There are little changes of the inner-ring bond lengths when donor ratio increases from one to two for the copolymers of quinoxaline with thiophene (Figure 4.2.11).

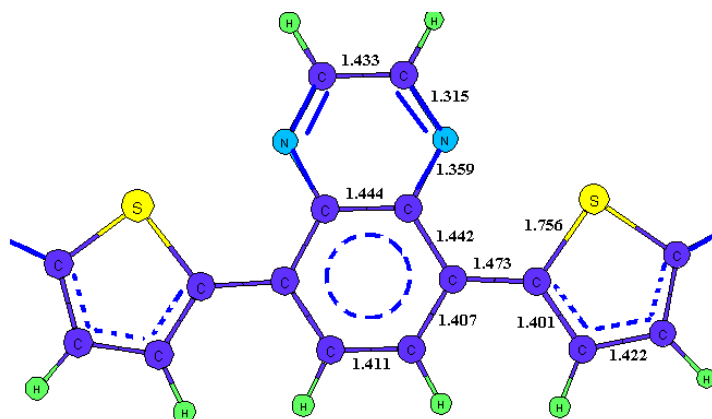


Figure 4.2.11 Optimized structures of inner rings of (Th-Qx-Th) co-oligomer

b) IPs, EAs, and Band Gaps:

Table 4.2.9 summarizes the IPs, EAs and band gaps of Th-Qx-Th co-oligomers with increasing chain length.

n, rep. unit	IP (eV)	EA (eV)	E _g (eV)
1	6.3	2.9	3.4
2	5.8	3.1	2.7

Table 4.2.9 IPs, EAs and E_g values for Th-Qx-Th co-oligomers

When, we increase the donor ratio of Qx-Th co-oligomers from one to two, HOMO energy levels increase and LUMO energy levels decrease, thus band gaps decrease.

Our theoretical data agree with experiments. (UV-VIS spectral data: λ_{\max} = 405-407 nm (3.06-3.05 eV) for monomer.

4.2.2.4 Poly [pyrrole-quinoxaline-pyrrole] , P(Py-Qx-Py)

a) Geometries:

Bond length alternation is 0.021 \AA for Py-Qx-Py co-oligomers; this value was 0.024 \AA for 1:1 donor-acceptor ratio of Py-Qx co-oligomers. The bond lengths do not change considerable amount when donor ratio increased from one to two at the copolymers of quinoxaline with pyrrole (Figure 4.2.12).

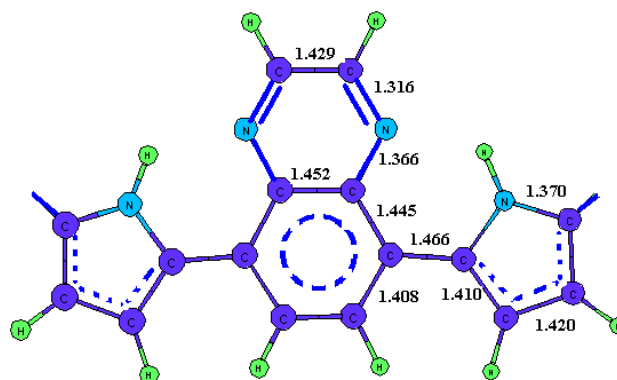


Figure 4.2.12 Optimised structures of inner rings of (Py-Qx-Py) co-oligomer

b) IPs, EAs, and Band Gaps:

Py-Qx-Py co-oligomers have lower IP and higher EA values than 1:1 donor-acceptor ratio of Qx-Py co-oligomers. Therefore, they have smaller band gaps (Table 4.2.10).

n, rep. unit	IP (eV)	EA (eV)	E _g (eV)
1	5.8	2.8	3.0
2	5.3	2.9	2.4

Table 4.2.10 IPs, EAs and E_g values for Py-Qx-Py co-oligomers

The absorption maxima of the monomer corresponding to P(Py-Qx-Py) is 502 nm (2.47 eV)^[53].

Chapter 5. Analysis and Conclusions

5.1 Homopolymers:

For homopolymers band gap order is : F-PThP < PThP < PQx. This order is consistent with acceptor power of systems.

The ground state of PThP is about 2.2 kcal/mol more stable in the quinoid form, this value increases to 3 kcal/mol for F-PThP, PQx is aromatic in the ground state. Thus, while quinoid character increases, band gaps decrease.

The bond length alternation (BLA) data are not consistent with the band gap results. The expected BLA order is the F-PThP < PThP < PQx, however, BLA results are: PQx (0.050 Å) < PThP (0.070 Å) < F-PThP (0.071 Å). Thus, band gaps do not correlate with BLA in homo polymers, then we investigated co-polymers.

5.2 Copolymers :

According to the donor-acceptor concept, combining two systems, one with a high-lying HOMO and one with a low lying LUMO, in principle, should decrease the band gap and increase the band widths, simultaneously. Thus, if we know the energies of the LUMOs of the acceptors and of the HOMOs of the donors, we may predict the band gap order of the studied copolymer systems. The order of energy difference of LUMOs of acceptor and HOMOs of donors are:

PPy - F-PThp (0.2 eV) < PTh-F-PThp (0.9 eV) < PPy-PThP (1.0 eV) < PPy-PQx (1.3 eV) < PTh-PThP (1.7 eV) < PTh-PQx (2 eV).

So, we might expect the similar band gap order with above order. However, we found a different order:

PTh-PThP (1.2eV) ~ PPy-PThP (1.2 eV) < PTh-F-PThp (1.4 eV) < PPy-PQx (1.8 eV)

This result is in contradiction with donor-acceptor concept.

According to energy levels, PPy is better donor than PTh. So, according to the donor-acceptor concept, one can expect smaller band gaps and wider band widths of PPy co-oligomers relative thiophene. However, P(ThP-Th) and P(ThP-Py) copolymers have the same band gaps and conduction band widths.

Due to our results, donor-acceptor concept is not correct in assertion of a claiming that copolymers with repeat units originated from a donor with high lying energy levels and an acceptor with low lying energy levels have narrow band gaps and wider band widths. The donor-acceptor concept can, sometimes, be used for decreasing the band gaps of the polymers while sacrificing the dispersion of the bands.

All copolymers have smaller BLA than the homopolymers. The smallest BLA (0.024 \AA^0) is evaluated at Qx-Py co-oligomers. However, Qx-Py copolymer has largest band gap (1.8 eV). Therefore, we might come to a similar conclusion as far homopolymers: the effect of BLA for the lowering the band gaps of narrow band gap copolymers is not the most important factor.

The ground state of P(ThP-Th) has an about 2 kcal/mol more stable aromatic form, the corresponding value is the 3 kcal/mol for P(ThP-Py). Thus P(ThP-Py) should have a larger band gap than P(ThP-Th) because it has a smaller quinoid structure contribution to the ground state of the polymer. However, the band gaps of both copolymers are equal.

In our calculations, we found lengths of inner-ring of co-oligomers are between the lengths of inner-rings of homo oligomers. e.g., ThP and Th homopolymers have 1.39 \AA^0 and 1.46 \AA^0 inner-ring bond lengths, respectively. They form ThP-Th copolymer, which has 1.45 \AA^0 inner-ring bond length. But HOMO-LUMO energy levels are affected significantly with forming co-oligomers. For instance, band gaps of PPy and PThP homo polymers are 3.2 eV and 1.4 eV, respectively, and the band gap of the copolymer P(ThP-Py) is 1.2 eV. This value is not average values of homopolymers.

P(ThP-Th), P(ThP-Py), P(F-ThP-Th) and P(F-ThP-Py) copolymers are composed of donor and acceptor moieties, however, P(Qx-Th) and P(Qx-Py) systems are composed both of acceptor groups. Thus, we expect larger band gaps and narrow band widths for acceptor-acceptor groups. Our results are consistent with this expectation.

In summary, I tested several concepts that are usually invoked in rationalizing band gaps of conducting organic polymers. Band gaps and band width are not quantitatively correlated with the energy difference between donor and acceptor units. Although BLA seems to contribute to the observed band gaps, there was not found a quantitative correlation.

Finally, geometrical mismatch between aromatic and quinoid repeat units forces geometry distortions that impose smaller band gaps. Overall, the situation is more complicated than simple concepts imply and further studies are needed before a final conclusion can be reached.

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